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PLASMOIDAL HIGH-FREQUENCY OSCILLATORY DISCHARGES IN "NON-CONDUCTING" VACUA

By R. W. Wood
Physical Laboratory, Johns Hopkins University

(Received February 17, 1930)

Abstract

Plasmoidal discharges. A new type of vacuum tube discharge is described, excited by comparatively low voltage high-frequency oscillations (1.7 meters up to 30 meters wave-length) in which remarkable luminous balls, spindles and pear-shaped bodies are formed. These have been reported in earlier papers in Nature and the Phil. Mag. A study of the conditions under which these bodies are formed and their behavior in magnetic fields has lead to the conclusion that surface charges play a part in their formation. They have been shown to be built of excited molecules, as their spectra are molecular band spectra (O_2 or CO) and since Langmuir has seen in their formation the possibility of plasma oscillations, such as he observed in the mercury arc; they have been named "plasmoids" provisionally.

Red phosphorescence of the glass wall. This occurs in all of the tubes containing oxygen at very low pressure. It appears to be due to low velocity secondary electrons in combination with excited oxygen. Its behavior in magnetic fields has been studied, and it appears when a plasmoid is deflected against the wall by a magnet. The red phosphorescence does not appear until after the high frequency discharge has operated on the glass for some minutes, becoming finally a bright ruby red. The same glass surface phosphoresces green under the impact of high velocity electrons given off from the inner surface of the glass when the external cathode is excited by higher voltages. It may happen that superposed streaks of red and green phosphorescence may occur simultaneously and they can be separated by a magnetic field.

Clean-up effects. Remarkable clean-up effects have been observed, it being possible to have a tube sealed off from the pump which can be made to show either a pure Balmer spectrum of atomic hydrogen (purple discharge) or the green discharge of molecular oxygen. The pressure changes occurring in the sealed off tubes as the type of spectrum changes have been followed with a vibrating quartz fiber manometer.

Spectroscopic investigation. The spectra of the plasmoids, their dark sheaths, and the less luminous gas in which they are imbedded have been investigated by projecting their images on the slit of a spectroscope. The band spectrum of molecular oxygen is seen in the whole tube, but is concentrated in the plasmoids and diluted in their dark sheaths; atomic lines appear as well, the local concentration being different for singly and doubly ionized oxygen.

General nature of discharge. There are two types of discharge, one at very low potentials, suggesting the Townsend discharge (unmodified by space or surface

charges) and a more brilliant one which comes in suddenly as the potential is gradually raised. Plasmoids, however, appear to form with both types, though their shape and distribution in the tube changes as we pass from one type to the other. External electrodes are used in all cases.

IN THE Philosophical Magazine for October, 1929, I gave a short account of some phenomena exhibited by very highly exhausted tubes, excited through external electrodes by comparatively low voltages, at a frequency corresponding to a four meter wave. References were made in this paper to earlier work by Kirchner, who first drew attention to the circumstance that, what is usually called a non-conducting vacuum, is excited to bright luminosity by these very high frequencies at comparatively low potentials. During the past autumn I have made a more careful study of these discharges with an oscillator having a wave-length of 1.75 meters built by A. L. Loomis at his laboratory in Tuxedo, New York, and later on in my own laboratory with other oscillators and sources of high potential. The investigation concerned the general nature of the discharges, their behavior in magnetic fields, and the spectra emitted by them, as well as the very remarkable "clean-up" effects shown.

In the earlier paper reference was made to the curious luminous bodies, balls, spindles and pear shaped forms, which usually appeared in the tubes, and it was shown that these luminous masses were formed of singly ionized molecules, either of oxygen, showing the band spectrum, or CO showing the so called "Comet-tail" spectrum, now known to be due to singly ionized CO molecules. Kirchner's original theory to explain the production of a luminous discharge with a potential of only a few hundred volts in a vacuum impervious to the potential of a large induction coil, was that, at these high frequencies, the electrons made "to and fro" excursions ("pendelt") under the rapidly alternating electric force, increasing enormously their chance of ionizing the rarefied gas by collisions.

While I feel convinced that an oscillatory motion of the electron takes place in the discharges, it appears probable that the matter is more complicated than imagined by Kirchner, for the discharges occur equally well when the position of the electrodes and the dimensions of the tube are such as to make these long to and fro excursions impossible.

It seems highly probable that the comparatively heavy ions remain practically at rest, and the circumstance that the luminous bodies are shown by the spectroscope to be built-up of ionized molecules, while the less luminous regions show atomic line spectra, made it appear probable that a careful study of the movements of these bodies under magnetic and electric forces would throw some light on the nature of the discharge.

It is very probable that surface charges on the glass play a large part, for as I showed in an earlier communication, the deflection of the electrons by a magnetic field, as indicated by the movements of the ruby red phorescence patches on the inner wall indicated electrons moving away from the electrodes in their vicinity, and towards the electrodes at the opposite

ends of the tube, the electrodes being near the middle. The end of the tube acted as if it had become a secondary cathode. Surface charges are also indicated by the curious circumstance that if the tubes fail to respond to the oscillator, they usually light up immediately if brushed once with a bunsen flame, or even if a lighted match is brought close to them. We thus have a vacuum tube which can be lighted with a match! I have frequently observed the discharge initiated by striking a match at some distance from the tube the effect being due probably to a modification of the surrounding field. In the earlier work sufficient care was not taken to insure a clean inner surface of the tubes, and the presence of CO masked the clean cut effects obtained in the present work.

We will now consider briefly the phenomena exhibited by one of the tubes during the process of exhaustion and subsequently. A tube of soft glass 2 cm in diameter and 30 cm long is blown round at one end, drawn down at the other for sealing, and exhausted with a Holweck molecular pump. The wires from the oscillator are wound once around the tube, forming ring electrodes. The character of the discharge is profoundly modified by very slight changes in the position of the electrodes as will appear presently. The tube was very carefully cleaned with a boiling solution of KOH followed by chromic acid before sealing it to the pump. When the discharge is first started the spectroscope shows a mixture of nitrogen and hydrogen, the former disappearing as soon as the tube is heated, the water-vapor liberated from the glass driving out the nitrogen. At first the color of the discharge is pink, and the spectroscope shows the secondary spectrum of hydrogen as well as the Balmer lines, but after ten or fifteen minutes of operation, the tube being strongly heated from time to time the color changes to the "fiery purple" characteristic of atomic hydrogen.

At this state it may happen, if the electrodes are properly placed, that the discharge shows periodic changes of intensity, along the tube, as shown in Fig. 1a.

The intensity change is not very marked in the case of hydrogen, but, as we shall see presently with only oxygen in the tube, we may have the condition shown in the lower figures, the spindle shaped luminous bodies giving an appearance suggestive of stationary waves. We may heat and pump continuously for an hour or two, no visible change taking place, the color remaining intense purple, and only the Balmar lines showing in the spectroscope. That we have a nearly pure atomic hydrogen (purple discharge) in a tube at very low pressure with well baked walls, is undoubtedly due to the fact that the very high frequency discharge keeps the hydrogen thoroughly dissociated into atoms. A low frequency discharge under these conditions is nearly white, with the secondary spectrum strong, due to the catalyzing action of the walls as shown in an earlier paper. If now the tube is sealed off from the pump and the discharge continued, a most remarkable change occurs in a few seconds. The color changes to pink and the spectroscope or a direct vision prism shows that the oxygen bands in the red-green part of the spec-

trum are developing rapidly and the Balmer lines fading away. In two or three minutes the last trace of hydrogen vanishes, and the color of the discharge is now bright green. It is important to note that the transition from pure hydrogen to pure oxygen occurs only after the tube has been sealed from the pump, which means that a slight rise of pressure is necessary. An explanation of this very remarkable behavior will be given presently. If the tube is joined to the pump by a fine capillary, the oxygen may develop before the sealing off process, for the pressure in the tube will be higher in this case than with a wider connecting tube. The green luminous bodies are now strongly developed and their position and shape alters with every change in the position of the wire ring electrodes, a change in position of one of them of only a millimeter, giving a complete redistribution as shown in Fig. 1, b and c.

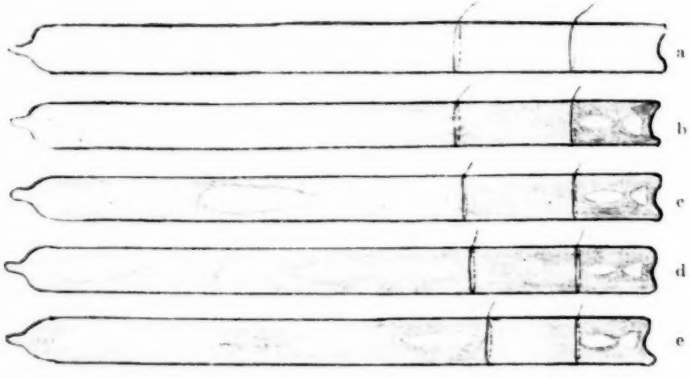

Fig. 1. Appearance of plasmoidal discharges under various conditions.

The tube shown in Fig. 1, b-c was flattened at one end and sucked in, producing a dome shaped bottom, like a wine bottle. This was done to see whether the form of the luminous body would be affected by the contour of the inner surface. A flattening of the green spindle was observed, as shown in the figure. An attempt was made to determine the effect of a change of length of the tube, with fixed electrodes by means of a sliding partition, (a short glass tube closed at one end which fitted snugly within the discharge tube) but a discharge formed on each side of it. A tube was then made with a glass partition fused within it, at the center, each half being exhausted separately. With ring electrodes near one end ,*both* compartments were excited to equal luminosity, i.e the glass partition served as an electrode quite as well as the wire rings. The excitation of the second compartment was not due to a stray field, as it appeared only when the wire electrodes encircled the other end of the tube.

The glass near the electrodes phosphoresces with a ruby red color, which is very intense, if the tube has been well baked and thoroughly exhausted. If the baking has been less complete the phosphorescence may not appear.

In this case the green discharge is usually brighter, but the spindles and balls are less pronounced.

Red Phosphorescence of Glass Wall.

The red phosphorescence of the glass walls of electrically excited vacuum tubes appears to have been first noticed and studied by Lilienfeld whose papers will be found in the Verh. der Deutsch. Phys. Ges. for 1906–1907. It was observed independently by the author some years later in the long tubes used for extending the Balmer series of hydrogen when oxygen was admitted to them. Gehrke and Reichenbeim attributed it also to oxygen, while Lilienfeld considered it due to slow cathode rays, associated with some other undetermined factor, and from certain observations on the magnetic deflection, considered the hypothesis of positive electrons.

In my own study of the subject with tubes excited in a very different manner from that employed by Lilienfeld and, at the time, in ignorance of Lilienfeld's observations, I arrived at first at quite similar conclusions, and frequently remarked that things would be much simpler of explanation if we could admit the existence of positive electrons! Further study however showed that these were not required, and I believe that progress has been made towards the solution of the mysterious red phosphorescence, though there are still points that require further investigation.

In the first place it has been found that high speed electrons, from a single exterior electrode showered with high potential sparks produce a green fluorescence of the glass in tubes containing oxygen at low pressure, the red phosphorescence being produced by electrons of probably lower velocity, when the electrode is attached to one pole of the high frequency oscillator, operating at comparatively low voltage. In this case no green phosphorescence is observed, but in the former case red phosphorescence in general appears in regions of the tube bombarded by secondary cathode rays of presumably lower electron velocity. I feel convinced also that the presence of excited oxygen molecules in contact with the glass walls is also necessary as will appear presently. This may be the unknown factor mentioned by Lilienfeld.

The glass, moreover, must be acted upon by the discharge for some seconds or minutes before the red phosphorescence appears. In one case a streak of green phosphorescence appeared when the discharge was first started, the color changing to red after a few seconds of operation. If the tube was then rotated on its long axis, so as to bring an "untreated" portion of the glass into the electron stream, the green color appeared again, changing presently to red as before.

If a bright discharge is produced at one end of the tube with a single ring electrode until the glass phosphoresces with a red color, and the ring is moved to the other end of the tube, we have no phosphorescence there, although the discharge is of the same character as before. It is evidently associated with a chemical alteration of the glass.

Character of Discharge and "Clean-up" Effects

The duration of the exhaustion, the amount of baking of tube while on the pump, and the operation of the discharge during the pumping, profoundly influence the subsequent behavior of the tube. With a tube of soft glass joined to the pump by a wide capillary (2 mm) the pumping was continued for 3 hours, during which time it was heated with a bunsen flame about twenty times. The discharge was operating most of the time, the color being intense purple (pure atomic hydrogen). When sealed from the pump, the spectrum changed to one of pure oxygen with about ten minutes of operation. After standing over night the discharge, when first started, was again fiery purple, only the Balmer lines showing, which presently faded away and were replaced by oxygen bands and lines, the color changing to green. This process was repeated over and over again, the transition from oxygen to hydrogen, being accomplished in many cases in a minute or two by heating the tube. We thus have a tube with which we can demonstrate either the spectrum of atomic hydrogen or molecular oxygen at will! With continued repetition of the experiment it was found more and more difficult to obtain the hydrogen stage, and the tube finally reached a condition in which only oxygen bands were shown, and the character of the discharge indicated a higher pressure. Heating the tube caused a momentary trace of the hydrogen lines with the oxygen bands but they faded in a few seconds.

I believe that this behavior may be explained as follows. While the tube is on the pump the oxygen and hydrogen formed by the dissociation of water-vapor coming from the glass, are continuously removed allowing fresh water-vapor to come out of the walls. The spectrum is therefore the line spectrum of hydrogen, which always appears with a discharge in water-vapor at low pressures. A few oxygen lines of relatively feeble intensity appear as well.

If now the tube is sealed off from the pump the pressure rises until a point is reached at which no more water-vapor escapes from the glass, and the hydrogen, formed by the discharge is driven into the glass by the discharge, leaving pure oxygen in the tube. This results in a lowering of the pressure, so that more water-vapor can escape from the wall, if the tube is allowed a rest of a day or two, or heated slightly and we again get the hydrogen lines, until all of the freshly formed hydrogen has been driven back into the glass. Repeating the process over and over again gradually raises the pressure of the oxygen in the tube, water-vapor escapes in smaller quantities and it becomes increasingly difficult to get the hydrogen spectrum as has been mentioned. The alternative explanation of the slow return to the hydrogen state would be to assume that it is the hydrogen and not water-vapor that comes out of the glass. If this were so, the gradual rise of pressure with repetition of the experiment would not occur. A different sequence of events was observed in tubes very thoroughly baked out in an electric furnace.

A tube of Pyrex glass, baked during the pumping operation, at a dull red heat for over an hour in an electric furnace behaved quite differently. This tube was not excited electrically during the exhaustion. When first subjected

to the potential of the oscillator there was only a very pale violet discharge, almost invisible. Red phosphorescence of the glass developed in a few minutes and presently a pale green ball (oxygen) appeared between the electrodes. Heating the tube caused the discharge to become brighter, and balls and spindles of green luminosity appeared but the hydrogen spectrum never appeared.

Study of Pressure Changes in "Sealed Off" Tubes with Quartz Fiber Manometer

It was obvious that a careful study of the pressure changes within the tube during these transitions was most important, and a number of tubes were prepared with quartz fiber manometers, (as used by Haber and Langmuir) by which the changes of pressure within the tube as a result of heating, electrical excitation, and repose could be followed.

These manometers are very easy to prepare, no graded seal being necessary. We have only to draw a fiber 8 or 10 cm long by hand (diameter about that of a very fine hair) drop it into the tube which has a round bottom like a test tube, heat the bottom to the fusing point and then quickly invert the tube, holding it vertical. The fiber will swing to the axis of the tube and remain firmly fixed to the glass. If it is off center, hold the tube horizontally and gently heat the glass at the point of attachment with a small flame until the fiber has sagged to the proper position. The fiber is illuminated by a lamp placed at the side and viewed through a low power microscope with micrometer eye-piece. By gently tapping the tube the fiber is thrown into vibration, and the time for the decrement to half amplitude taken with a stopwatch.

With a tube of soft soda-glass sealed off from the pump, after a one-hour pumping with the discharge operating continuously and repeated heatings (up to the appearance of the *D* lines of sodium) the color was fiery purple and the spectrum that of atomic hydrogen. This indicates water vapor at low pressure in the tube. The vibrating quartz fiber sank to a half amplitude value in 12 seconds. When on the pump the time for half amplitude decrement was 30 seconds. This showed that the pressure had risen after, or during the sealing off process.

The tube was now subjected to the high frequency discharge until the hydrogen spectrum was replaced by that of pure oxygen. The time for half amplitude decrement, which in future we will call H.A.D. was now found to be 30 secs, the same value as when on the pump. After operating for half an hour the time for H.A.D. had decreased to 15 seconds; showing that the oxygen pressure was increasing. The tube was now gently heated with a flame. Purple discharge of hydrogen and time of H.A.D. 7 seconds. Ran discharge until only pure oxygen spectrum. Time of H.A.D. 15 seconds, as before heating.

The inference from these observations is that, under the conditions of these particular experiments in which prolonged heat treatment was not

given to the tube, water-vapor, liberated by heating the tube is completely "cleaned-up" by the discharge, while oxygen formed by the action of the discharge upon the glass or upon water vapor contained within the glass does not "clean-up" but accumulates in the tube with continued operation. This is not the case with a tube subjected to long heat treatment.

With a Pyrex tube the following results were obtained. At the start the spectrum showed both hydrogen lines and oxygen bands. Time of H.A.D 25 seconds. Heated until discharge white (Balmer lines and band spectra of hydrogen). Time of H.A.D. 4 seconds. We now have a relatively high pressure of water-vapor in the tube. Operating for 1 minute, time of H.A.D. 15 seconds. Operating for 5 minutes, time of H.A.D. 25 seconds. Oxygen spectra only. This indicates that *most* of the oxygen and all of the hydrogen of the original water-vapor present is driven into the glass by the discharge.

With a Pyrex tube baked in a furnace at a dull red heat, with the Holweck pump operating, for over an hour, the time of H.A.D. of the fiber was four minutes and 30 seconds! Discharge at first pale violet, with faint pink fluorescence of the glass. Red fluorescence developed in five minutes with faint green glow of oxygen in the tube. The time of H.A.D. was now 45 seconds. The elimination of water-vapor was evidently fairly complete in this case. Three days later the time of H.A.D. before starting the discharge, was found to have increased to 65 seconds. With the discharge operating the time was 90 seconds, and after running for half an hour it was back to 65 seconds. After 2 1/2 hours of operation by the discharge the time increased to 5 min. 40 secs., indicating a pressure as low as, or lower than when the tube came off the pump. After the lapse of several weeks, the oxygen discharge was strong (green plasmoids) and the time of H.A.D. was eight seconds, which changed to 45 seconds after a one minute operation on the five meter oscillator.

These results show that in a well-baked out tube the oxygen "cleans-up" but that it appears again after the tube has stood for some time, or been subjected to heat. The liberation of oxygen by heat and its rapid "clean-up" by the discharge can be repeated over and over again. Nitrogen and neon, introduced into the tube were rapidly cleaned-up.

General Nature of the Discharge

Langmuir, from his study of the oscillations which occur spontaneously in a mercury vacuum arc excited by a low voltage direct current, developed a theory based on the hypothesis that a cloud of ions served as a medium in which electrons could oscillate to and fro with a frequency dependent on the density of the ions (i.e. the number in unit volume). A region filled in this way with ions and electrons he called a "plasma," and he suggested to me that very probably the phenomena shown by my tubes were closely related to those which he had observed with the mercury arc. The circumstance that the spectroscope shows that the luminous balls, spindles and pear shaped bodies are made up of singly ionized molecules, identifies them with Lang-

muir's plasma, (at least this is a plausible hypothesis to make), and on this account I propose, for the present at least, to call them *plasmoids*.

Before taking up in detail the subject of the type of discharge in which the plasmoids are formed, it will be well to consider some effects observed in the same tubes when operated by high potentials of lower frequency, as with hammer interrupter, or intermittent in which the character of the discharge is quite different. Some of the phenomena manifested can be considered to advantage in any effort to formulate a theory of the "plasmoidal" discharges.

Discharge by "Leak-Tester"

This apparatus, sold for therapeutic purposes, and used in physical laboratories for hunting for leaks in vacuum systems, generates a rapidly alternating intermittent potential sufficient to produce a shower of sparks an inch or more in length from its single terminal to any earthed conductor. Excitation of the highly exhausted tubes by this apparatus results in phenomena quite different from those observed with the high-frequency sets.

If the single electrode is applied to the under wall of the tube near one end a patch of green fluorescence is observed above it, and two strips of *red*

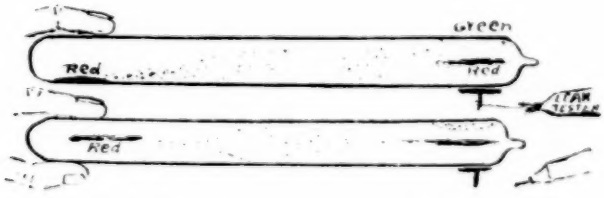

Fig. 2. Red and green phosphorescence patches. Low frequency excitation.

phosphorescence appear along the sides of the tube half way between the electrode and the green patch as shown in Fig. 2. Figs. 2, 3, 5, 7, 12, 13 and 14 are reproduced as "negative" i.e. bright parts of the discharge are black.

If the finger is touched to the upper wall at the opposite end of the tube, a patch of red phosphorescence appears below it on opposite wall. If the thumb is then applied to the wall over the red patch, two red streaks appear on the sides of the tube, half way between the thumb and finger, and if a third finger is applied over one of these it disappears at once and the remaining red streak in the opposite side becomes much brighter. These effects indicate that the red phosphorescence is caused by a discharge of some type, which initially filled the tube uniformly, but which is driven away from those parts of the wall which are "grounded" by an exterior electrode (the finger) and forced against the opposite wall. The depressed "discharge" appears as a faint green glow.

As a substitute for the two fingers and the thumb I wound a "grounded" strip of aluminum around three quarters of the circumference of the tube. The bright red streak appeared along the center of the gap and extended along the wall down the tube towards the electrode. Fig. 3, a.

If a wire, W held between the fingers, was brought up towards the red streak from below, the streak was deflected upwards spiraling around to the back of the tube Fig. 3b, while it was deflected downwards if the wire point was brought down from above. If the wire was touched to the outer wall exactly over the center of the red streak, it "forked" into a Y, the two branches curving around the wall and uniting at the back. Fig. 3c, very much as would a thin jet of water squirted along the inner wall, and divided into two jets by a small obstacle. The wire had little or no effect if brought up to the red streak in the region of the gap in the aluminum cylinder.

The red streak was also deflected by a magnetic field, upwards or downwards according to the direction of the field. Care was taken to ensure that this deflection was due to the field and not to the mere approach of the metallic mass. The direction of the deflection indicated electrons moving along the inner wall from left to right, i. e. *towards* the electrode.

The deflection by the magnetic field occurred only for that portion of the red streak beyond (to the right of the cylinder). The portion lying between the opposed edges of the 3/4 cylinder appeared to be held firmly fixed in posi-

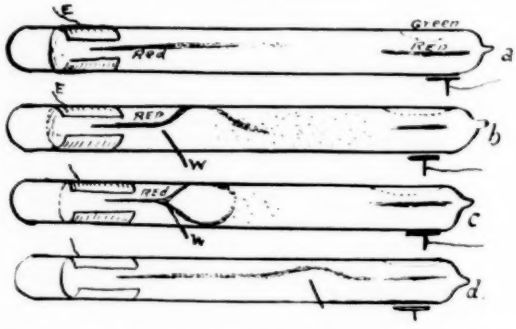

Fig. 3. Deflection of red streak of phosphorescence by grounded wire.

tion by electric forces, while the portion outside was free to move under the influence of the force applied by the magnetic field.

It is worthy of comment, in connection with the forking of the streak into a Y, when the point of a wire is placed over it, that the repulsive force due to the wire apparently exerts no influence on the electron (?) stream producing the red phosphorescence streak until it reaches the point immediately under the wire, and that the stream is not driven away from the glass wall towards the axis but merely divided laterally into two streams, which spiral around the tube wall in opposite directions, meeting on the opposite side.

The stream thus appears to have a tendency to stick to the wall, once it has been brought into contact with it by the electric forces set up by the grounded cylinder of aluminum.

In another tube in which the pressure was higher (?) the red streak was bent into an arc by the approach of the wire, i.e., the deflection occurred only in the neighborhood of the wire, as shown in Fig. 3, d. It seems possible that, in this case electron streams from opposite ends of the tube were uniting at the point near the wire. In this case the streak extended nearly down to the

leak-tester and was more sensitive to the approach of an earthed conductor. It was also possible to drive it off the wall entirely, by the approach of an earthed conductor directly above it. A very important observation was made with another tube fitted with the three quarter cylinder of aluminum, and excited at the other end with the leak tester.

The streak of phosphorescence of yellowish color extending out from the gap in the cylinder towards the electrode, appeared to be a mixture of both types, green and red superposed, the latter more easily deflected by the wire or magnet. As the wire was brought up, the red streak was pushed aside, leaving a green streak almost undisturbed, and the same thing could be accomplished with a magnet. When the two streaks were thus separated the original yellow color vanished, being decomposed into its constituents pure red and green. This seems to indicate that we have high velocity electrons giving the green streak, and low velocity electrons, in conjunction with oxygen, giving the red streak. The green streak was visible only in the immediate vicinity of the aluminum cylinder, while the red one extended down the tube nearly to the electrode. If the wire were approached to the tube immediately above the red streak near its end (i.e., at a considerable distance from the gap in the cylinder) it could be made to disappear from the wall and reappear on the opposite wall, the electron stream having been pushed across the axis of the tube. If however the wire was brought up at a point nearer the cylinder the deflected electron stream clung to the wall, curving around the inner wall as a spiral, as has been shown previously (Fig. 2, b).

Excitation by 30 Meter Oscillator

The excitation in this case was brought about by simply holding the tube partly within the large coil of copper ribband carrying the oscillatory current. Two large green plasmoids were formed, one at each end, with sharply defined rounded ends facing the ends of the tube and fading away gradually towards the center which were repelled by bringing up the finger to the wall. The tube contained only oxygen at fairly low pressure, but there was no red phosphorescence. On pushing the tube entirely within the coil the discharge vanished, showing that it had been excited by the electric field outside of the coil and not by electro-magnetic induction.

The same tube excited by the "leak-tester" showed only green phosphorescence of the glass with no trace of red. The tube was then excited by the two meter oscillator, and red phosphorescence developed in two or three minutes, accompanied by formation of green plasmoids. This result was due to a partial clean-up of the oxygen i.e., the vacuum was improved.

On exciting again with the leak-tester a red phosphoresence mixed with green in an irregular manner was obtained.

Introduced once more into the coil of the 30 meter oscillator, the projecting end being held with two fingers and the thumb, a single plasmoid formed, tapering to a point on the side towards the finger, and rounded on the end towards the coil. A streak of red phosphorescence formed on the

glass extending from the region between, but not covered by the fingers, to a point opposite the tapered end of the plasmoid. If now the end of a wire held in the fingers was brought up to the wall on the side opposite to that on which the red streak had formed, and near the pointed end of the plasmoid, the latter turned up and joined the red streak, i.e., it was repelled by the wire.

It seemed probable to me that the red streak produced by grasping the tube with the fingers was produced in each case at those moments at which the opposite end of the tube was anode. In the case of the excitation by the leak-tester it will be remembered that red phosphorescence streaks were produced at each end of the tube Fig. 2, a and Fig. 3, a.

If the above hypothesis is correct, the red streaks should not appear simultaneously but in alternation. Examination of an ordinary Geissler tube excited by the leak tester in a waggled mirror showed that its polarity alternated in unison with the vibrations of its small "hammer-break," but the light of the red streaks was not bright enough for a conclusive test in this way, the single images seen in the mirror being rather feeble. A stroboscopic method was therefore adopted, by which the tube could be observed at rest and continuously.

Stroboscopic Examination of Discharge

The tube was excited by connecting a single ring of wire, wound around one end of the tube with one pole of a 20,000 volt (60 cycle) transformer. The other end was furnished with an earthed three-quarter cylinder of aluminum foil, as before.

Red phosphorescence appeared close to the ring, and as a red streak in the gap of the cylinder. The tube was viewed through a slot in a card-board disk mounted on the shaft of a synchronous motor operated on the same 60 cycle circuit as the transformer. Only one red patch could be seen at a time, the one visible depending upon the position of the eye as it was moved around the circumference of the disk. This experiment appears to prove that in all of the experiments, in which, with a single electrode at one end of the tube, we have electrons moving from the other end towards the electrode, the motion occurrs only at the moments at which the electrode is anode. This applies also I believe to the high frequency experiments, in which plasmoids are formed, and should be taken into account in framing a theory of the formation of the plasmoids. Experiments were also made to ascertain how low a frequency would produce a visible discharge.

If the tube were placed between the poles of a small Holtz machine, no luminosity whatever appeared within the tube, though the potential was high enough to cause sparks to jump around the wall. This same tube, on the five meter oscillator with a potential sufficient to give a spark of only half a millimeter or less, showed a brilliant green plasmodial discharge. A small rotating commutator was now made by pasting tin-foil strips along the edge of a disk of ebonite mounted on the shaft of a small motor. By means of this the steady potential of the Holtz machine could

be converted into an alternating potential. Luminosity appeared within the tube with alternations as low as six per second and reached a maximum at about fifty per second. The discharge vanished as the speed of the commutator increased, for reasons which are not quite clear. Possibly the conductivity became so good that the machine could not build up potential.

The Plasmoids

The study of the plasmoids has been conducted along two quite different lines. (a) Their formation and the changes which they undergo when the form and position of the external electrodes are altered, and their behavior in magnetic fields have been very carefully investigated, with oscillators of different frequencies and with the gas at different pressures. (b) Spectroscopic data have been obtained in regard to the radiations emitted by the plasmoid, by its relatively dark sheath and by the more or less uniformly luminous gas in which it is embedded. It seemed probable that a determination of the distribution in space of singly and doubly ionized atoms and the singly ionized molecules, would be of help in ascertaining the physical processes involved in the plasmoid formation.

There appear to be two distinct types of discharge, one in which the luminosity of the gas is low and the other in which it is high. Plasmoids are formed in both cases, but the transition from one type to the other is abrupt.

This suggests perhaps a transition from a "Townsend discharge," to a glow discharge, space charges and charges on the wall being absent in the former, and the potential drop merely the normal drop from anode to cathode while the "glow discharge" results when ionization becomes more pronounced, and space charges are present.

The transition from one type to the other was well shown in the case of a very highly exhausted tube containing oxygen as the residual gas. It was furnished with two ring electrodes formed of single turns of fine wire wound tightly around the tube.

With the lowest potential capable of exciting a luminous discharge, a pale green disk shaped like a double convex lens appeared midway between the ring electrodes as shown in Fig. 4, a. As the potential increased the disk expanded to the form shown in Fig. 4, b, while a further increase of potential caused the sudden appearance in its place of a much brighter green plasmoid in the form of a prolate spheriod, Fig. 4, c. My first attempt to explain the formation of the plasmoids with their sharply defined smooth surfaces, was along the lines usually followed in accounting for the stratifications in gas discharges, namely that the plasmoid surface represented an ionization caused by electrons which had acquired the requisite velocity after leaving the cathode. This works out well for cases a and b of Fig. 4, for the equipotential surfaces of the ring electrodes are about as shown in Fig. 5 which is a cross section through the rings. At low potentials (as in Fig. 4, a) ionization does not result until the electrons have reached equipotential surfaces 1, and the lenticular luminosity appears in the region between them. At a slightly higher potential the electrons have acquired the requisite velocity

when surface 2 is reached, and the region between these surfaces is luminous as in Fig. 4, b. The sudden production of the spheroidal plasmoid at a slightly higher potential may result in part from the formation of negative

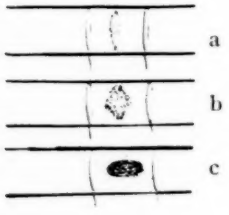

Fig. 4. Change in shape of the plasmoid with increasing potential.

charges on the tube wall between the electrodes, but the complete explanation in this case probably requires the introduction of other factors, such for example as the plasma oscillations imagined by Langmuir.

It appears possible that if we could apply a stroboscopic method to these very high frequency discharges we might find that the brilliancy at opposite

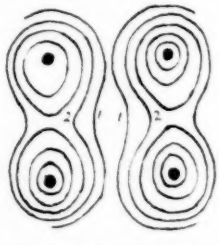

Fig. 5. Equipotential surfaces of ring electrodes.

ends of the plasmoid oscillated in unison with the discharge, i. e. the rounded ends facing the ring electrodes became luminous in alternation. My reason for considering this possible was the circumstance that in the case of a short tube excited by introduction into the helix of the thirty meter oscillator two plasmoids were formed as shown by Fig. 6. That these occur in alternation

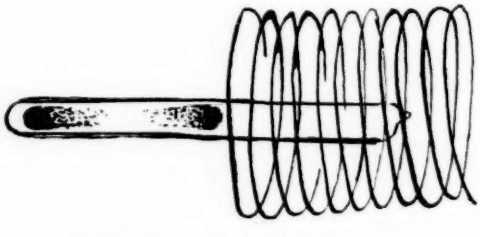

Fig. 6. Plasmoides formed with 30 meter oscillator.

and not simultaneously is indicated by the behavior of the discharge at low frequency as examined with the stroboscope. If now the conditions were such as to bring these plasmoids closer together we should have the single

spheroidal plasmoid referred to above. The tube in which the lenticular and spheroidal plasmoids formed was excited with the 1.75 meter oscillator by means of two disk electrodes applied on opposite sides of the tube as shown in Fig. 7.

These give a field of simple type, which is easy to calculate, with a potential sufficient to give a spark about half a millimeter long. With a potential giving a spark perhaps half a millimeter in length a brilliant green plasmoid shaped like a double convex lens appeared midway between the electrodes and parallel to them. Fig. 7, a. The plasmoid was surrounded by a dark sheath and two dark arches covered the electrodes as shown in the figure. As the potential was lowered by reducing the filament current, the lenticular disk contracted, remaining very bright however, but suddenly was replaced

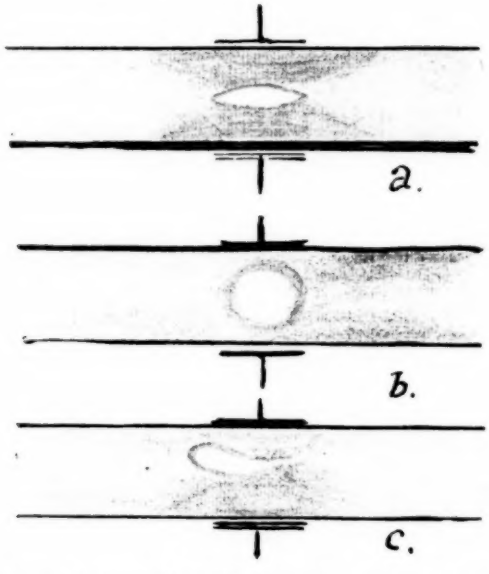

Fig. 7. Change in shape of plasmoids with decreasing potential and magnetic deflection of plasmoid (c).

by a sphere of low luminosity surrounded by a wide dark sheath. Fig. 7, b. If the pole of a small bar magnet was brought up to the wall, in the condition "a" the plasmoid was squeezed to one side and deflected upwards as shown in Fig. 7, c. The magnetic field was such as to deflect downward moving electrons to the left and upward moving ones to the right. The formation of the sphere and disk I am unable to explain.

The development of plasmoids at periodic intervals along the tube, as shown in Fig. 1, I was at first inclined to ascribe to a zig-zag reflection of the electrons from surface charges built up on the inner walls by electron impact. It seemed, however, highly improbable that such sharp localization could be produced in this way, or that a movement of one ring electrode through a distance of only one or two millimeters could cause such a change in the paths of electrons down the tube as to cause a complete redistribu-

tion of the plasmoids in space. Langmuir's theory that the plasmoids are oscillators having a definite frequency of vibration seems to be a much more promising line of attack.

Nevertheless, certain observations have been made which apparently show that a reflection in the manner imagined actually takes place. In a tube at very low pressure, containing only oxygen and excited by a single disk electrode placed close to the outer wall, the following phenomena were observed as the capacity of the condenser in the oscillatory circuit was increased from zero. It must be remembered that with the variable capacity set at zero, the circuit is practically interrupted and the potential is very low if oscillations are present at all. As the capacity is increased a patch of ruby red phosphorescence appears on the upper wall of the tube immediately over the disk, with an area considerably larger than that of the disk, and a second red patch on the lower wall of the same diameter as the disk, as shown in Fig. 8, a.

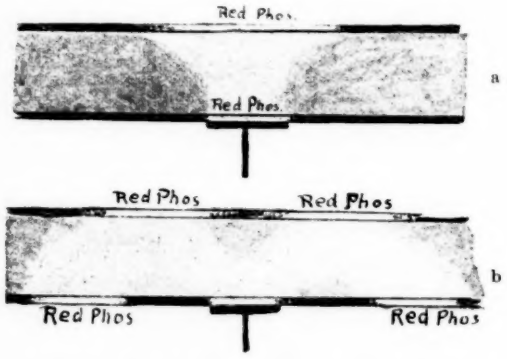

Fig. 8. Reflection of slow electrons by surface charge.

The only way in which I can account for the circumstance that the lower red patch exactly covers the region immediately above the disk electrode is to assume that some of the electrons moving along the lines of force, when the disk is negative fail to reach the upper surface before the field reverses and hence travel backwards along the reversed lines of force to their starting point.

The paths of the electrons through the gas is marked by a faint green luminosity. If the capacity is made slightly greater, which increases the potential, the upper red patch divides at the middle and spreads out, the glass ceasing to phosphoresce immediately above the electrode, and two new red patches appear in the lower wall as shown in Fig. 8, b.

The cause of the division of the electron stream over the electrode results perhaps from the formation of a negative surface charge immediately above the electrode, while the two lower red patches of phosphorescence, appear to be due to the downward deflection of the oblique streams of electrons by negative surface charges at the upper red spots. A slight further increment of capacity results in the sudden birth of two plasmoids to the

right and left of the descending streams. The reversal of the electron stream alluded to above was also indicated in a vertical tube so highly exhausted that practically nothing but red phosphorescence was observed, (with a disk-electrode at the bottom). In the upper two thirds of the tube and at the bottom upward moving electrons were found, while a strong downward stream was indicated by the magnetic concentration of red phosphorescence about one third of the way up. This stream appeared to me to be due to the pulling back of the tail end of the upward electronic blast, when the disk became anode. This case will be alluded to again presently.

If the oxygen is at a slightly higher pressure and we gradually increase the capacity in the oscillating circuit, we get a quite different sequence of events, and can watch the birth of a plasmoid. With a moderate capacity the discharge has the appearance indicated by Fig. 9, a.

Its color is yellow-green of much greater intensity than in the previous case and there is a dark arch over the electrode. The upper wall shows a feeble red phosphorescence, indicating that some of the electrons succeed in reaching it. There are also indications of a segmentation at *A*, which is

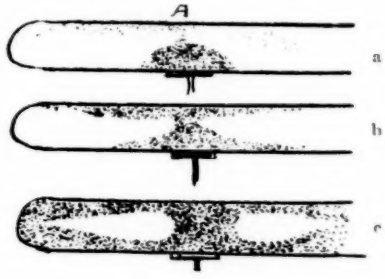

Fig. 9. Birth of a plasmoid.

destined to become the breaking point of the discharge when the plasmoid forms. If now a magnet pole is brought up from the side (of polarity such as would cause upward moving electrons to be deflected to the left) the portion *A* is squeezed to the left and a large and perfectly formed plasmoid develops Fig. 9, b and c.

With an oscillator of five meters wave-length, and a single disk electrode applied to the flat end of the tube the plasmoid development as the capacity of the condenser was increased is illustrated in Fig. 10.

The total capacity of the condenser was about 300 cm and the scale was graduated to equal divisions from 0 to 100. The capacity of the condenser is given below each figure. With the two smallest capacities, the discharge is of the first type and of a very feeble green color, the plasmoid having the shape of a spear-head.

Increasing the capacity to 11 causes a sudden increase in luminosity and two plasmoids form of the shape indicated. With capacity 16 the upper rounded end of the large plasmoid streams up to a point, and at capacity 20 a break to the brighter type of discharge occurs and two sharply defined plasmoids appear at opposite ends of the tube. Two rings of red phosphorescence

appear immediately above and below the lower plasmoid, due probably to reflection of the electrons from charges on the tube wall, or possibly to the upward electron stream from the disk cathode and the downward stream which occurs when the disk becomes anode, a condition mentioned a moment ago. If a magnet pole is brought up to the lower plasmoid, both plasmoids contract and disappear at the same moment, but if the magnet is brought up to the upper one it contracts and vanishes but the lower one remains unaffected.

I think it highly probable, in view of the stroboscopic experiments previously described, that the two plasmoids appear in alternation as the field reverses, the upper plasmoid appearing as a result of a negative charge on

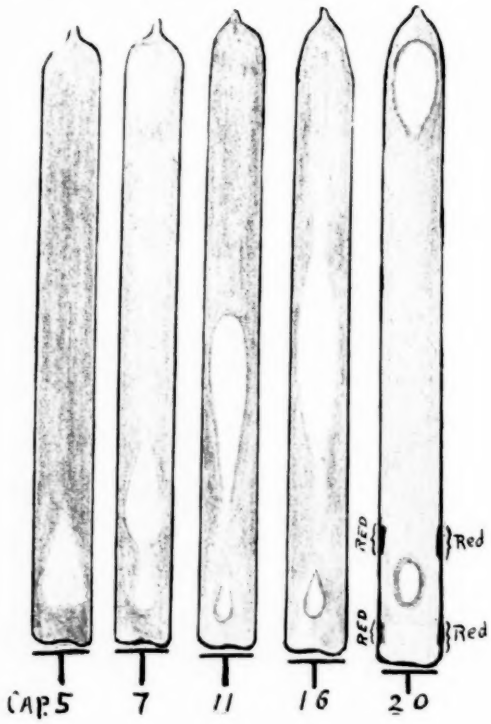

Fig. 10. Plasmoid formation with increasing potential.

the wall of the tube above it, at the moment when the electrode becomes anode. The application of the field at the lower end prevents the electrons, in part at least, from reaching the upper end of the tube, and this probably is responsible for the contraction and disappearance of the upper plasmoid.

The effects of a magnetic field on the plasmoidal discharge is very complicated, due, probably to the circumstance that we have electron streams moving in opposite directions but with different velocities at the same point in the tube. These streams do not of course occur at the same instant but in alternation as the polarity of the oscillator reverses, and they will be deflected in opposite directions by the field. This two-fold deflection is often observed at the center of the tube.

The magnetic field, in some cases, causes the plasmoids to shrink and disappear, in others it causes the birth of plasmoids where none existed previously. It has been found extremely difficult to systematize the multitude of different effects observed, or draw any very definite conclusions from them, and only a few selected examples will be given. The others will be kept on record, as they will be of value in testing any theory of plasmoid formation that may be developed subsequently. It will be best to begin with what appears to be the simplest case, a tube containing oxygen at such low pressure that scarcely any trace of plasmoid formation occurs. The pale green discharge filling the tube quite uniformly, when excited by a single disk electrode at the base and the five meter oscillator. A small U-shaped magnet was used, much larger than shown in the figure in such a position that the lines of force were perpendicular to the paper in Fig. 11. The intens-

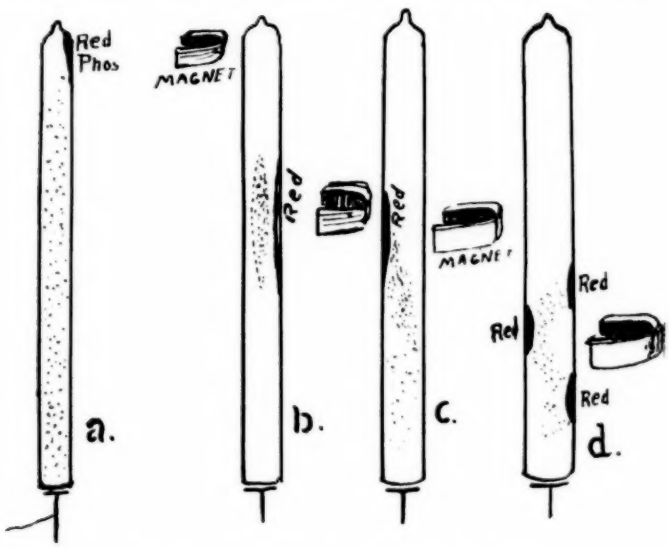

Fig. 11. Magnetic deflection of discharge.

ity of the luminosity fell off gradually towards the top of the tube where it was practically zero. The top of the tube showed a faint red phosphorescence, which was deflected to one side when the magnet was 20 cm from the tube, the direction of the deflection indicating upward moving electrons. On moving the magnet down the tube it was necessary to bring it up closer to cause red phosphorescence on the wall. This indicated that the upward moving electrons had a higher velocity half way down the tube than at the top, due perhaps to a reversal of the field direction during their flight from the disk cathode towards the top of the tube. A small plasmoid formed along the axis of the tube in this stage Fig. 11, b. On bringing the magnet closer to the tube a bright red patch formed on the opposite wall below the magnet, indicating electrons moving down, the plasmoid disappeared and the luminous discharge was pressed against the wall terminating at the spot of red phosphorescence. Fig. 12, c. The inference appears to be that we have at

this point, electrons moving down with a velocity a little greater than that of the electrons moving up, the streams occurring in alternation of course.

On moving the magnet down the tube, two red patches formed on the right hand wall, and one on the left half way between them, Fig. 11, d, and the discharge appeared to zig-zag across the tube as shown. This case is more complicated, and I cannot account for it by considering simply two electron streams moving in alternation in opposite directions with different velocities.

Appearances suggest the formation of surface charges and reflection of the electron streams as in a former case (Fig. 8, b.). Some of the effects described above might be explained by assuming upward moving electrons along the inner wall, the downward stream being at the center, but this seems improbable. We will next consider the case of a tube with oxygen and CO at low pressure in which a white plasmoid formed at the top of the tube with its head pointing downwards as shown in Fig. 12, a.

If the pole of the bar magnet was brought up from behind towards the tail of the plasmoid, it disappeared when viewed from the front but was still visible when viewed from the side, due to its having been spread out

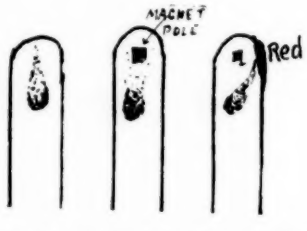

Fig. 12. Magnetic deflection of plasmoid.

into a fan. This would indicate electrons moving both up and down. No phosphorescence of the glass was observed. On bringing the magnet closer a new sharply defined tail formed, and the head of the plasmoid was pulled up; at the same time the tail bent to the right, finally touching the glass forming a patch of red phosphorescence on a closer approach of the magnet. Downward moving electrons were indicated in this case.

With the magnet still closer to the tube a faint red patch appeared on the left hand wall, below the magnet, due to upward moving electrons.

If the magnet was approached immediately below the plasmoid, or even below the bulbous expansion of the tube, the plasmoid contracted and vanished, without suffering displacement.

When the magnet was brought up to the plasmoid shown in Fig. 10, Cap. 11, the upper end was deflected to the right and the lower end to the left red spots forming on the wall, indicating electrons streaming out from the center of the plasmoid through its upper and lower surface. In this case the discharge was of the first type (Townsend?).

In other cases the magnet indicated electron streams flowing into the opposite ends of the plasmoid. Elongated plasmoids were constricted or broken into two, by the magnetic field the broken ends being deflected in

opposite directions against the wall forming red spots, the indication in this case being electron streams flowing out of the broken ends.

It has not been found possible to systematize these observations, doubtless due to the fact that the field, by deflecting electrons, establishes a new condition in the tube (destruction or rupture of a plasmoid and a redistribution of surface charges) and the effects we observe are those produced by the field on this modified discharge. In general I have found that whenever a plasmoid is pushed against the wall by a magnet red phosphorescence is produced.

In the condition shown in Fig. 10, Cap. 20, if the magnet pole is brought up from behind the upper plasmoid, the plasmoid slowly collapses to a point and disappears, red phosphorescence appearing on the left hand wall indicating electrons moving down. The oxygen pressure was higher in this case than in one previously mentioned, in which an upward electron stream was found in the upper two thirds of the tube.

Spectroscopic Study of Plasmoidal Discharge

In this study an image of the discharge was focussed on the spectrograph slit, so that a point-to-point correspondence obtained. It was found that the spectrum of the faintly luminous discharge in which the plasmoids were immersed, (with pure oxygen only in the tube) showed the bands of the

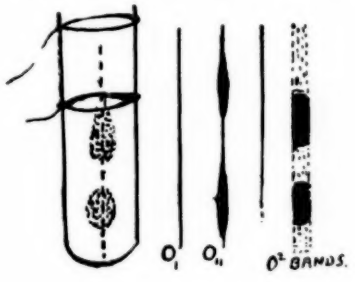

Fig. 13. Distribution of intensity in spectrum lines and bands.

oxygen molecule, and the atomic lines due to OII and OI. The discharge in the single case which we shall consider was produced with the 1.7 meter oscillator with two wire ring electrodes, the plasmoids having the form shown in Fig. 13. The slit covering the portion shown by the dotted line. In this diagram the local intensity of a line is roughly indicated by its width. The atomic line due to OI was of uniform intensity throughout its length, the OII lines showed a slightly greater intensity in the vicinity of the plasmoids, two lines (oxygen triplets) between the green and blue bands were of uniform intensity except at the bottom of the tube, where they were very faint, while the bands due to oxygen molecules were much more intense in the plasmoids, the intensity decreasing abruptly at the plasmoid surface. This shows that in the plasmoid we have a concentration of excited oxygen *molecules*, while the concentration in its dark sheath is less than in the luminous discharge in which it is embedded.

IONIZATION OF HELIUM BY POTASSIUM POSITIVE IONS

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Abstract

A continuation of previous attempts to ionize gases by positive ions has been extended to helium using potassium positive ions as high as 750 volts accelerating potential. At pressures between 0.01 and 0.1 mm there is definite evidence of ionization of helium above 150 or 200 volts accelerating potential. The effect is much smaller than in the gases previously reported, but it may be distinguished from the secondary emission of electrons from the metal parts under action of the positive ions. Great difficulty was encountered in changes of intensity of ionization due to impurities in the helium. Some of the uncertainties in previous work have been removed by changing the relative positions of electrodes.

IN A previous paper by one of us[1] evidence was offered for the ionization of argon and neon by potassium positive ions. It was determined that these positive ions could produce ionization which was distinguishable from other effects produced upon the metals in the tube when the accelerating potential was in excess of 150 volts. An inherited error in calibration of the McLeod gauge used for pressure measurement caused a misstatement in that paper regarding the pressure range over which the effect of ionization is found. The pressure range is nearer 0.005 to 0.1 mm which partially obviates the argument concerning unusually long mean free paths of the positive ions. The indication is that their paths are comparable with, but slightly longer than, the mean free path calculated from kinetic theory data.

This work has been extended to the study of helium in a new tube using electrical connections practically the same as previously described. Fig. 1 shows the tube with its electrical connections. The chief features in which it differs from the previous tube are (1) a ground glass joint by which filament changes may be more easily effected, (2) greater space between collector S and grid G from which the products of ionization are collected, (3) a flat plate P placed only 2 mm above the grid G and parallel to it. The ground glass joint is made in two parts, the upper part being coated with graphite, the lower portion coated with stopcock grease and sealed with mercury. A vacuum connection between these two parts minimizes the danger of stopcock grease entering the tube. The filament and cathode leads are mounted in this joint so that the filament may be easily removed and recoated with Kunsman catalyst. The cathode is, as before, a steel cylinder completely enclosing the filament; however, the channel through which the positive ions emerge into the upper part of the tube has been made smaller (1.5 mm diameter) and the hole in the collector through which it projects has been

[1] R. M. Sutton, Phys. Rev. **33**, 364 (1929).

made smaller (3 mm diameter) so that the field between collector and grid is more uniform. By placing the grid 2.5 cm above the collector S, a larger region is available from which to collect the products of ionization. Furthermore, the region above the grid is greatly reduced from the previous case so that the amount of ionization produced between the grid and upper plate has a negligible effect upon the plate current (I_p) of positive ions. It was found that the reflection of positive ions from the plate was extremely small or negligible so that the V-shaped plate previously used to reduce reflection was eliminated.

The helium used was obtained in moderately pure form from the United States Bureau of Mines at Amarillo, Texas. It was further purified by passing over oxided copper turnings and charcoal in liquid air until it was spectroscopically pure. As an additional precaution, the helium was passed through

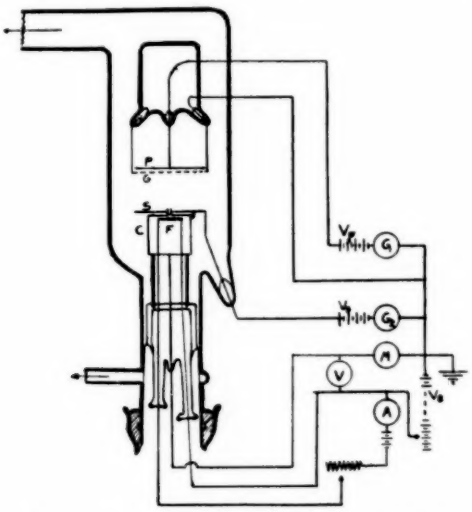

Fig. 1. Experimental tube and connections.

a magnesium discharge tube before its introduction into the experimental tube. The ionization properties of the gas seem to be particularly sensitive to impurities, increasing very materially with amounts of impurity which must be only a few percent of the total gas pressure. It is desired to study this aspect of the ionization more carefully in the future under controlled conditions. Until now, however, the effort has been to work with the purest gas obtainable. Consequently, whenever the gas gave indication of contamination by reason of marked increase of ionization without measurable change of pressure, it was rejected and fresh gas was admitted to the apparatus. This increase may be due in part to ionization of impurities by collision with helium excited by positive ion bombardment.[2]

The system of measurement consisted in directing the potassium positives through the narrow channel in the cathode into the region between the col-

[2] G. P. Harnwell, Phys. Rev. **29**, 683 (1927).

lector S and plate P. The potential of S was maintained 20 volts positive with respect to the cathode (ground) thus preventing positive ions from reaching the collector directly. Any electrons liberated from the grid or from the cathode under impact of the positive ions would reach S in case they had such initial direction as to enter the field of this collecting potential V_s. It was found that the long narrow channel used in these experiments was the source of a rather large amount of secondary emission of electrons to the collector, especially when the channel was contaminated with potassium from the filament. The secondary emission was, in general, about three times as great as it was in the previous tube. Any electrons liberated by ionization of the gas between S and G are collected on S and show themselves as an additional current in excess of the secondary emission. The primary positive current is measured on the plated P, which is also kept positive (18 volts) to prevent the escape of secondary electrons from the plate into the region between S and G. It will be seen that nei-

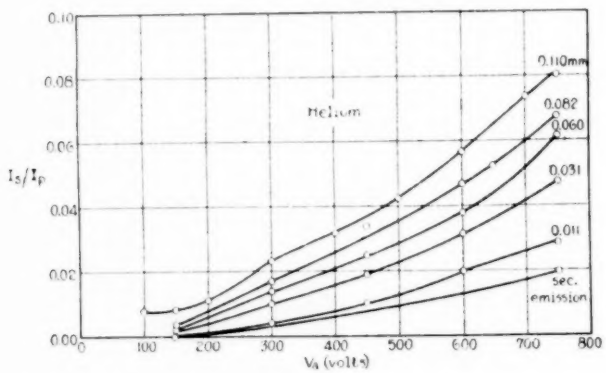

Fig. 2. Ionization in helium at various pressures. Ratio of electron current to collector to positive ion current to plate as function of accelerating potential of positive ions.

ther of these collecting potentials can give electrons energy sufficient to ionize helium and by making the plate potential $V_p = 18$ volts, it was possible to prevent escape of electrons from the plate due to photoelectric effect from radiation produced by excited helium atoms. However, these collecting voltages which are higher than those used in previous work with gases of lower ionizing potentials are in excess of the ionizing potentials of most gases except helium; hence they may be a source of ionization by electrons when impurities are present.

In general, the current to the collector S was measured with a gas pressure of less than 10^{-5} mm and then, without changing other conditions, it was again measured with helium present. A series of measurements of the current to S at different accelerating potentials was made at each gas pressure used, and fresh helium was introduced for each new pressure test. Figure 2 shows a series of curves obtained at various pressures by plotting the electron current to the collector (I_s) divided by the positive ion current to the plate (I_p) as a

function of the accelerating potential of the positive ions. Each curve thus represents the efficiency of ionization at various accelerating potentials for each pressure shown (after subtraction of the current due to secondary emission). The lowest curve was taken with pressure 10^{-5} mm or less. It represents the effect of secondary emission alone. The lowest pressure at which a distinguishable effect due to the presence of helium can be detected is 0.01 mm at which the mean free path of K^+ in helium is approximately one-half the distance between the collector and grid. From .01 to 0.1 mm there is definite evidence of ionization. It will be seen from Fig. 2 that the ionization current plus the secondary emission at 0.11 mm amounts to 8 percent of the initial positive ion stream at 750 volts, and the secondary emission with no gas present is equivalent to approximately 2 percent of this current, which leaves 6 percent as the part due to ionization of the gas assuming that the secondary emission is independent of gas pressure. (This assumption may need some modification inasmuch as the secondary emission in the cathode channel may increase due to scattering of the initial positive beam against the metal). We have no way of determining at present how many impacts each positive ion makes between the collector and grid, so that we are not free to predict or calculate the probability of an impact resulting in ionization. However, it appears to be rather small considering that the positive ions at 750 volts have many times the kinetic energy necessary to ionize helium.

There has been some question as to whether the nature of the discharge through the channel into the upper region of the tube does not change materially with the presence of gas in the tube. This point has been tested by measuring the total current between the cathode and filament under all operating conditions of the tube; the only change in this current due to increase of accelerating potential of the positive ions is such as may be adequately accounted for by the increased secondary emission from the cathode itself under action of the ions up to the potential at which an arc occurs. It is possible, however, that a few positive ions of helium might be formed within this region due to electron impact, and these may emerge into the upper region of the tube to cause collisions with the gas present. It is doubtful whether any such collisions would result in ionization, since the escape of an electron from the combined attraction of two positive helium ions cannot be effected as easily as the escape from the field of a K^+ and an He^+ ion. The chief effect of such helium positive ions in the original beam would be to increase I_p, whereas a decrease in I_p is noted with the presence of the gas. This decrease of I_p upon the introduction of gas may be attributed to a slight cooling of the filament due to conduction, or to retardation of the ions by collision with gas molecules sufficient to prevent their reaching P against the retarding potential of V_p of 18 volts. That part of the decrease of I_p due to stoppage of the initial positive ions obviously causes an abnormally large calculated ratio I_s/I_p. This is particularly evident in the curve for 0.11 mm which does not approach zero as rapidly as do the curves taken at lower pressures. The relatively high ratio at 150 volts is due to almost complete stoppage of the initial positive beam, rather than to a greater amount of ionization at this pressure.

A comparison of results obtained from the present tube with those previously reported was made in a test run on neon. Taking due account of the change of position of electrodes and the increased secondary emission in the present tube, the two tubes give quantitative results in good agreement. Figure 3 summarizes the evidence for argon, neon, and helium. N is the number of electrons per initial positive ion per cm path at 1 mm pressure, calculated at the average of the pressure range, 0.05 mm.[3] The increase of N with pressure indicates the possibility of ionization of more than one gas atom

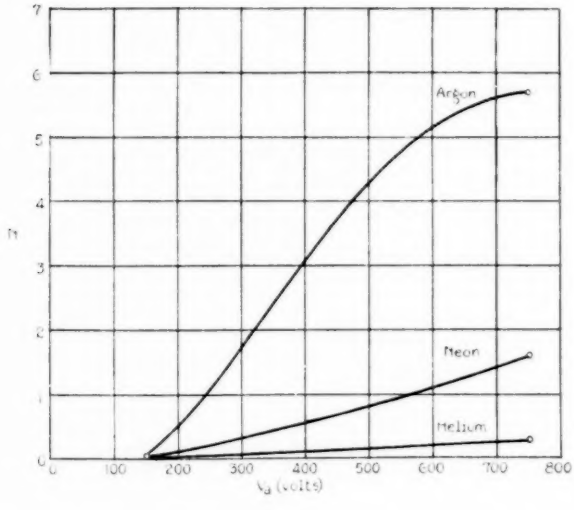

Fig. 3. Comparative ionization of argon, neon, and helium by potassium positive ions. N represents the number of ions formed per positive ion per cm path at 1 mm pressure.

by a single positive. At 0.1 mm pressure each positive ion encounters approximately 15 collisions over a path 3.4 cm long on kinetic theory data. This penetration of the positives is not as great as that previously adduced, due to correction of the pressure measurements, but is still comparable with the magnetic analysis experiments of Durbin, Kennard, and Dempster.[4]

The present work will be continued on the investigation of other gases and different positive ion sources. It seems desirable also to test further the effect of impurities upon ionization of the noble gases.

[3] K. T. Compton and C. C. Van Voorhis, Phys. Rev. **26,** 436 (1925).

[4] F. M. Durbin, Phys. Rev. **30,** 844 (1927); R. B. Kennard, **31,** 423 (1928); A. J. Dempster **31,** 634 (1928).

ON THE POTENTIAL RELATIONS IN THE STRIATED POSITIVE COLUMN OF ELECTRICAL DISCHARGES THROUGH HYDROGEN

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Abstract

The many lined visible spectrum from the striae in the positive column of a discharge through hydrogen must arise from electronic transitions between excited states having energy levels differing by only about 3 volts for the violet lines. The assumption made by others that the light arises from transitions to the ground level from the lowest excited state of 11.5 volts cannot hold because such transitions would give light in the extreme ultra-violet region only. It is necessary to produce excited states at least 3 volts above the lowest excited level. This requires an energy not far below the ionization potential of 16.1 volts. A process is described by which both excitation of molecules to the required levels and ionization might occur at equal intervals throughout the positive column, but a difficulty arises in the fact that the voltage drop between striae under certain conditions is found to be several volts below the ionization potential. It is assumed that the electrons acquire enough energy for ionization in these cases from collisions of the second kind with molecules of some impurity which are in excited states of comparatively low energy levels. Reasons are given for believing that the impurities involved come from the walls of the discharge tube, and that the walls play a very important role otherwise, as well.

THE periodic changes in the electric force along the length of a striated positive column in a discharge tube are usually taken to indicate that there are periodic positions along the column where ionization is taking place. In fact J. J. Thomson[1] postulates that when the positive column becomes striated it does so because under the given circumstances the periodically changing field which accompanies the striated condition permits the replenishment, with the least total expenditure of energy, of the electrons lost along the path of the discharge either by diffusion to the walls of the tube or by attachment to positive ions or neutral molecules. We should accordingly expect the energies acquired by electrons between striae to correspond at least to ionization potentials.

However, the main part of the light coming from the positive column does not have its origin in the recombination of ions, for there is strong evidence[2] that there is but little recombination in the body of the gas between electrons and positive ions, owing doubtless to the high prevailing speeds of the former. Such union occurs rather at the walls of the tube.

The light from striae in a discharge through hydrogen gives a many lined spectrum and must originate then in *molecules* in excited states. The

[1] J. J. Thomson, Phil. Mag. **8**, 1 (1929).
[2] See R. Seeliger, Phys. Zeits. **30**, 329 (1929).

existence of the periodic changes of light intensity which distinguishes the striated state of the positive column points to the energy acquired by electrons between striae as that corresponding to an excitation voltage. Indeed Grotrian[3] using a stream of electrons from a hot cathode in mercury vapor has observed a striated discharge with periodic changes of potential of 4.9 volts, corresponding to the lowest excitation level of mercury. Here, however, there was no ionization occurring throughout the volume of the vapor.

When a cold cathode is used ionization as well as excitation of molecules must be taking place in the positive column and there is then a question how the two effects requiring different voltages are produced at the same equal space intervals along a discharge tube. It seems reasonable to assume that the process requiring the higher energy on the part of the electrons, i.e. ionization, determines the potential fall between the striae, and that the excitation of molecules and subsequent radiation from them is an accompanying action of this first process. According to this view when the electrons in their progress through the field have acquired enough energy for excitation some of them will begin to have inelastic collisions with molecules which raise these to excited states. This action will continue until the electrons which have as yet had no collisions of this kind gain enough energy for ionization after which both kinds of inelastic collisions will take place in the same region along the tube. The probability that at any one impact the collision of an electron with a molecule will be an inelastic one is small and hence the process given is a possible one.

The actual linear distance along a discharge tube in which the above two actions take place need be but a minor part of the whole distance between two striae since the energies required for ionization of a hydrogen molecule and for its excitation to states from which visible light may result are not greatly different. To this is added the fact that the mobility of an ion varies inversely as its motion of agitation and so when the electrons have acquired the most energy from the field their progressive speed along the tube will be the least. Accordingly many more impacts than elsewhere will here occur within a given length of the discharge tube and nearly all of the electrons will have their inelastic collisions inside a short length of the tube from which they will then begin a new excursion. Some addition must be made to this process because under some conditions the potential drop between striae is less than the ionization potential.

Compton, Turner and McCurdy[4], who have expressed views regarding the process of stria formation which in some respects are similar to those above, have assigned an important role to impurities in the gas which are so essential for the appearance of striae in nearly all gases. They postulate that the function of the impurities is, by collisions of the second kind, to restore to the stable form such metastable excited atoms which, having diffused to all parts of the interstria spaces, would otherwise after inelastic impact with comparatively slow electrons give rise to radiations there and thus tend to wash out the visibility of striae.

[3] W. Grotrian, Zeits. f. Physik **5,** 148 (1921).

[4] K. T. Compton, L. A. Turner and W. H. McCurdy, Phys. Rev. **24,** 597 (1924).

Günther-Schulze[5] also visualizes the procedure by which the electrons in a discharge tube give up their acquired energy in inelastic impacts within periodic narrow zones in much the same way as that described above, but inasmuch as under some conditions the fall of potential between striae is less than the ionization potential he assumes that the ionization process is not related to stria formation and that ionization arises from a separate set of fast electrons evidence of whose existence has been given from spectroscopic data by Seeliger and Ôkubo.[6] Günther-Schulze believes that striae are formed as a result of the inelastic impacts in the narrow zones named of a slower set of electrons which raise the molecules to the lowest excitation level; and seeks support for this view from the fact that under some conditions the energy acquired by electrons between striae in hydrogen has a value nearly equal to this excitation potential. Unfortunately an excitation of molecules to the first levels in hydrogen does not suffice to explain the luminosity of the striae which is observed, as will be shown below.

A comparison of the magnitudes of the energies required for the ionization and for the excitation of hydrogen molecules with the measured potential drops between striae evidently deserves special consideration.

The ionization potential of the hydrogen molecule, which takes place without dissociation, is given[7] as 16.1 ± 0.2 volts and the energy required to raise a hydrogen molecule to the lowest excited level is given as 11.5 ± 0.4 volts. Above the lowest excitation level there are a large number of other levels extending according to Richardson[8] to about 15.1 volts.

In the light from striae the visible part of the spectrum must result from transitions between excited states since a transition from any excited state to the $1^1\Sigma$ state would give a line far down in the ultra-violet. To obtain the violet end of the spectrum we must start with an excited state at least 3 volts above the lowest excited level of 11.5 volts, i.e. at 14.5 volts or more.

In some recent measurements[9] I found the potential drop between striae in hydrogen at pressures below 0.5 mm to be approximately 12 volts and even lower values have been obtained by others. If in this region of pressures the electrons possess only the energy gained directly from the field between adjacent striae, how then is it possible for them to ionize the molecule or to excite it to a sufficiently high level to give rise to the visible spectral lines which are observed? It might be urged that perhaps the ionization in the gas is confined to molecules of traces of impurities having a lower ionization potential than those of hydrogen, but the argument cannot be used to explain directly the production of a hydrogen spectrum. It seems necessary therefore to invoke the aid of some other process. We might postulate, since the electrons are not able to obtain the requisite energy in the potential drop between adjacent striae, that they carry energy from one stria distance into the next,

[5] A. Günther-Schulze, Zeits. f. Physik **31,** 1 (1925).
[6] R. Seeliger and J. Okubo, Phys. Zeits. **25,** 337 (1924).
[7] Geiger and Scheel, Handbuch der Physik, Vol. 23, p. 749.
[8] O. W. Richardson, Proc. Roy. Soc. **A125,** 23 (1929).
[9] J. Zeleny, Jour. Franklin Inst., **209,** (1930).

only a part of them losing their energy by inelastic impact in any one stria. It is difficult, however, to imagine how such a process could bring about a periodic appearance of light.

It seems more plausible to assume that the electrons get the energy needed for ionization or excitation, over and above that acquired from the field within a single stria distance, by collisions with molecules of some impurity which are in an excited or metastable state requiring less energy than is requisite to excite a hydrogen molecule. There is good theoretical ground and some direct evidence[10] for the possibility of an electron having its energy increased by this sort of a collision of the second kind. By the presence of traces of impurities of different kinds and in different amounts might be explained the widely different minimum values obtained for the potential drop between striae under different circumstances and by different observers.

In support of the above view it may be mentioned that Pentscheff[11] found in very pure hydrogen that, while the potential fall in a stria diminished with reduction of pressure for a constant current, it at no time got below 20 volts, whereas in slightly impure hydrogen it fell to 13 volts under the same circumstances. The pressures used are not stated but if the lowest values of the potential which are given were obtained at pressures below 1 mm, the energy gained between striae by electrons in pure hydrogen were more than sufficient for the ionization of hydrogen molecules, whereas in the impure hydrogen it is necessary to assume that the electrons acquired some energy from secondary processes, such as the one described above, to explain the observations.

Then too, my recent measurements show that when the hydrogen gas was kept stationary and not renewed the energy acquired by electrons in their passage through a stria at any pressure is one to two volts less than when the gas in the discharge tube was being continuously renewed. We should expect a larger amount of impurity to be present in the gas in the first case cited since impurities dislodged from the walls of the tube by the action of the discharge would accumulate in the tube when the gas was not being renewed.

The amount of foreign gas liberated from the walls would naturally depend within some limits on the magnitude and time of action of the discharge current, and according to the view expressed above the potential fall between striae should accordingly diminish as the discharge current is increased. This is actually in accord with my own observations as well as those of Holm, Wehner, and Neubert.[12]

Pentscheff[11] also found a decrease in the potential fall between striae with increase of current when impure hydrogen containing mercury vapor and other gases coming from the walls of the tube was used, but when very pure hydrogen was used and great care taken by prolonged treatment to free the

[10] See H. D. Smyth, Proc. Nat. Acad. Sci. **11,** 679 (1925).

[11] P. B. Pentscheff, Phys. Zeits. **7,** 463 (1906).

[12] R. Holm, Phys. Zeits. **9,** 558 (1908); F. Wehner, Ann. d. Physik **32,** 49 (1910); P. Neubert, Ann. d. Physik **42,** 1454 (1913).

metal parts and the walls of the discharge tube of occluded impurities the potential fall between striae rather increased somewhat as the discharge current was increased.

Again, when discharges of the same current density are sent through two tubes of different diameters we might expect the amount of impurity liberated per unit surface of the walls to be approximately the same and inasmuch as the larger of the tubes has a larger ratio of volume to surface the concentration of the impurities liberated from the walls would be greater in the smaller tube. We should then expect the potential fall per stria to be smaller in the smaller tube, and this was found to be the case in my recent measurements.

When the pressure of the gas in a discharge tube is increased a discharge through the tube is less effective in liberating occluded impurities from the walls and such as are liberated form a smaller proportion of the gas than would be the case at a lower pressure. If the amount of these liberated impurities tends to decrease the potential fall between striae then this fall should decrease with decrease of pressure and such was the relation I actually found[9] both with a stationary gas and with the gas flowing continuously through the discharge tube.

Neubert[12] found that when all spectroscopic traces of mercury disappeared from the discharge through hydrogen the potential fall between striae was 11 volts at the lowest pressure used although previously when this condition was not fulfilled the values obtained were as low as 7.5 volts. Mercury molecules which appear in this instance to lower the potential fall between striae in hydrogen do not possess excitation levels low enough to account for the facts in all cases. However among other likely impurities to be found in discharge tubes there is for example oxygen whose molecules possess metastable states of energy less than 2 volts.

The evidence which has been presented in favor of the view that the liberation of impurities from the walls of the discharge tube by the current is an important factor in determining the variations of the potential fall between striae which have been observed under various conditions, is to be sure for the most part circumstantial evidence.

In connection with the experimental result that the energy acquired by electrons in their motion between two striae increases as the pressure increases, it should be emphasized that there is evidence which indicates that electrons in collisions with molecules may lose more energy than would result from purely elastic collisions and which loss alone I considered in computing the energy acquired by electrons from the observed potential fall between striae. By such greater losses if of the proper magnitude might be explained the increase with pressure in the observed potential drops between striae, but the assumption of these larger losses introduces other difficulties and does not help to explain most of the other observed variations studied.

Another factor that may have some influence on the striated discharge consists of the gas convection currents always present in these discharge

tubes. It is believed however that most of the causes that affect distances and potential drops between striae center about the walls of the tube. These walls, under electronic bombardment during a discharge or with change of pressure or temperature, release occluded molecules of the principal gas and those of foreign substances. They destroy the metastable states of molecules which impinge upon them. They are the seat of the main portion of the recombination of ions and electrons which occurs in the discharge tube, giving rise thereby to electric currents from the axis of the tube towards these walls. Electric charges which collect on the walls influence the electric field in the neighboring gas; and electrons in collision with the walls may lose more or less of their energy depending on the state of the surface of the walls. The differences between the numerical results of different observers on stria distances and the potential fall between striae in discharge tubes can best be accounted for by assuming them due to effects of different conditions at the walls of the tubes. Full equilibrium conditions at the surface of these walls are at best very slow of attainment especially where the gases inside of the body of the glass are concerned. Even if by special treatment such an equilibrium is attained and concordant results obtained in a given case, the nature of the essential elements in equilibrium might still remain unknown.

ON THE DISTRIBUTION IN TIME OF THE SCINTILLATIONS PRODUCED BY THE α-PARTICLES FROM A WEAK SOURCE

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Abstract

The course of radioactive transformation, which in all known cases takes place in strict conformity with an exponential law of decay, is most satisfactorily explained on the supposition that individual atoms disintegrate in complete independence one of another, so that the disintegrations throughout an extended source constitute a perfectly random series of events. Many observations favor this conclusion, but experiments have recently been described showing that at high concentrations (Kutzner) and also at very low concentrations (preliminary work of Pokrowski) departures may occur. An experiment is here described in which the record of more than 10,000 scintillations produced by the α-particles from a weak source of polonium has been obtained and analysed. A large solid angle was effective, as in Pokrowski's experiments. The various corrections to be applied to the immediate data are discussed: in the present case they were of no importance. There was no evidence to show that the Marsden-Barratt distribution formula was not completely valid under the conditions obtaining.

An investigation was also made of the effect of intense γ radiation on the rate of disintegration in a weak source (Pokrowski), with entirely negative results.

Introduction

A SERIES of exactly similar point-events separated from one another in time but limited to a prescribed small region of space is defined as a "random" sequence when the probability of occurrence of one such event is the same for equal small intervals of time irrespective of the temporal locations of those intervals. For series comprising point-events separated in space as well as in time, or of line-events having a common focus whilst being separated in time, a further condition must be satisfied if the events are to be considered as taking place "completely at random." In the former case, in any given interval of time, the probability of occurrence of a single event must be the same for equal small elements of volume, irrespective of the spatial locations of such volume elements—and, in the latter, equal probablities must characterise equal small elements of solid angle about the focus no matter what the directions of the axes of the elementary cones considered.

Radioactive disintegration in an extended source of active material may be regarded as a phenomenon involving line-events originating in foci themselves distributed in space. Now, macroscopically examined, all such cases have been found to exemplify a common transformation law and the customary interpretation of this fact has been based on the assumption that,

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in as far as concerns its time relationships, the ultimate atomic process occurs entirely at random. If this be assumed then the spatial distribution of disintegrating atoms in an extended source must also be a random one—and the observed distribution of directions of particle (or quantum) emission likewise random, for here, whilst preferential directions with respect to natural atomic axes are not excluded, in any practical case the random distribution of atomic axes in space would completely mask such regularities if in fact they were present.

Whilst this is the logical conclusion to be drawn from the usual interpretation of exponential decay, where the analysis is carried down to the behavior of individual atoms, it has been variously maintained that the phenomena observed on the macroscopic scale require no further "explanation" than that the time-distribution of disintegrations in a radioactive source, considered as unit, shall be a random one. From this point of view there remains the possibility that the complete randomness which we have considered may be found lacking under a more penetrating analysis. However unsatisfactory such a contention may appear, from the physical standpoint—and whether or not we hold the view that it is even permissible when the whole range of macroscopic experiments is considered[1]—the fact remains that a number of careful experiments has been made and that some of them point to departures from a time-randomness under certain conditions of observation.

For the type of statistical analysis here involved two methods are available, based upon the Bateman[2] and the Marsden-Barratt[3] formulae respectively. In either case a graphical means may be employed in the final comparison of experiment with theory, and, when this is done, conclusions appear more obviously in the latter case, since theoretically a linear function is predicted. But the Bateman type of analysis possesses the compensating advantage that a numerical criterion is afforded of goodness of fit by the dispersion coefficient which may be calculated from the experimental data themselves. Both methods have been used in practice. Kutzner[4] has made a very thorough analysis of the data afforded by three series of observations automatically recorded under as nearly as possible identical conditions of operation of an electrical point counter. The sole difference between the series (which had reference to 7761, 6907 and 5923 particles, respectively) lay in the surface concentration of polonium in the radioactive source employed. Here there was a factor of 25 times as between conditions in the first and third series, the actual concentrations being roughly 2×10^{-4}, 8×10^{-4} and 5×10^{-3} equivalent milligrams per cm^2, respectively. With the weakest source no appreciable deviation from perfect time-randomness

[1] In the writer's opinion the only evidence which the macroscopic experiments fail to supply is evidence for the random distribution in space of the disintegrating atoms in a given source. The exponential law of decay may be deduced alike from measurements made on the radiation emitted within a small or a large solid angle about such a source.

[2] Bateman, Phil. Mag. **20,** 704 (1910).

[3] Marsden and Barratt, Proc. Phys. Soc. Lond. **23,** 367 (1911).

[4] Kutzner, Zeits. f. Physik **44,** 655 (1927).

was found, but, with the other two, deviations quite outside the limits of probable error were set in evidence. In each case dispersion was subnormal (Bateman analysis), there being a marked lack of the longer time intervals between observed disintegrations (Marsden-Barratt analysis). The extent of the discrepancy increased with the surface concentration in the source. Whilst leaving the full interpretation until fresh data had been obtained using large solid angles (only about 1/400 of the total emission was originally employed), Kutzner concluded that his results were in agreement with those of Curie,[5] who found complete accord between experiment and theory with polonium sources of (apparently) very small concentration. The experimental material in this latter case consisted of 9974 measured time intervals belonging to four distinct series of measurements.

Recently Pokrowski[6] has published an account of preliminary observations with very weak sources and large solid angles. The concentration employed was about 10^{-7} equivalent milligrams per cm^2. It is not stated what material was used. Data having reference to 1633 time intervals, analysed by the method of Marsden and Barratt, showed an excess both of the very short and the very long intervals and no real agreement with theory over any appreciable range. In the discussion it was pointed out that new phenomena at small concentrations might be expected if at the higher concentrations mutual action between neighboring nuclei was possible. On account of the fundamental nature of such a suggestion, and because a suitable source of polonium of small concentration was readily available, it was thought worthwhile to make a series of observations parallel to those of Pokrowski, using the scintillation method of registration as he had done. Moreover, the writer did not feel compelled to make the present investigation exhaustive—covering a wide range of surface concentrations—most especially because it is explicitly stated by Pokrowski that his report is merely preliminary in scope. Rather is it intended to put forward this restricted series of results, only, as independent evidence, for what it is worth.

Experimental Method and Results

As a source of α-particles for scintillation experiments polonium is in many respects most suitable: it is not accompanied by appreciable β or γ radiation, and its period is sufficiently long for the decay generally to be negligible. However, when experiments extending over a number of weeks are in question, the latter condition no longer holds[7] and the desired constancy can be retained only by employing sources of radium *D*, *E* and *F* in equilibrium. Now the writer possessed some pieces of gold leaf exposed to radon in May 1929.[8] In January 1930 calculation showed that their α-

[5] Curie, J. Physique **1,** 12 (1920).

[6] Pokrowski, Zeits. f. Physik **58,** 706 (1929).

[7] The type of "uncorrected" distribution of time intervals which would be obtained in the Marsden-Barratt analysis of data referring to a source of varying activity is one in which very short and very long intervals are each in excess of the number calculated theoretically for a constant source of the same average activity.

[8] See Feather, Proc. Camb. Phil. Soc. **25,** 522 (1929).

particle activity was still increasing—but sufficiently slowly for this material to be considered a constant source of α-particles for the present type of experiment over a period of two or three weeks.[9] It was decided, therefore, to employ it in the work to be described. By placing the gold leaf directly in contact with the zinc sulphide screen a solid angle of approximately 2π radians could simply be attained. Preliminary tests showed, however, that the activity of the source was 5 or 10 times too great for convenient counting. A reduction was made as follows: one surface of a flat piece of glass was very lightly ground with fine emery. A small piece of the activated gold leaf was placed upon the ground surface and, by means of the smooth rounded end of a glass rod, used as a small pestle, was gradually ground to an extremely fine deposit of gold dust which adhered to the roughened surface. The zinc sulphide screen, supported on a microscope cover glass, was then fastened in position in contact with the ground surface. On the free upper surface of the cover glass was fastened a piece of thin aluminum foil, pierced with a hole of approximately 1 mm^2 area, which served to limit the portion of screen under observation. The microscope used was built up of a Watson's Holoscopic objective, of numerical aperture 0.45 and focal length 16 mm, and a low-power eyepiece, giving a field of view of about 8 mm^2 area. The source system was supported so that the hole in the aluminum foil was central in the field of view and, during periods of observation, a dim red light produced a faint illumination of the foil, leaving the central portion of the field relatively dark.[10] The mean interval between scintillations was somewhat greater than 3 sec.[11]

The record itself was made with the aid of a drum chronograph with magnetically controlled pen, the drum being driven at a uniform rate by the combination of falling weight and centrifugal governor. The uniformity of rate was tested from time to time and found altogether satisfactory. Throughout the presentation of the results, for sake of simplicity, time intervals have been replaced by linear intervals; the conversion factor from the one to the other is 0.921 cm/sec.

Observations were spread over thirteen consecutive days; on each day two or three "sessions"— 30 "sessions" in all. During each session "periods of observation" alternated with periods of rest, each, on the average, about a minute and a half in length: in all, 334 "periods of observation." During each period about 30 scintillations were recorded; altogether 10134 "intervals" between scintillations were measured. In the treatment of the records periods were measured to the nearest millimeter and the number of intervals in each period was counted. From this material the mean interval, ω, was determined. Intervals were measured in millimeters and entered in a statistic according to their length. In the first analysis grouping was in millimeter ranges, the elementary group containing those intervals of which

[9] A more complete statement on this question is reserved for the discussion.

[10] Cf. Chariton and Lea, Proc. Roy. Soc. **122A,** 304 (1929).

[11] From the figures given by Pokrowski it would appear that his field of view had an area of about 70 mm^2 and that the mean interval in his experiments was roughly 0.8 sec.

the length lay between x and $x+1$ mm. Later these groups were combined in sets of three and values of n_x obtained, where n_x now represents the number of intervals of length between $x-1.5$ and $x+1.5$ mm. Values of N_ξ followed immediately from this series of numbers; here N_ξ is the number of intervals of length greater than ξ mm. Now the formula of Marsden and Barratt may be written

$$N_\xi = N_0 e^{-\xi/\omega} \tag{1}$$

or

$$\log_{10} N_\xi = \log_{10} N_0 - (0.4343/\omega)_\xi. \tag{2}$$

In our case $N_0 = 10134$ and $\omega = 31.28$ mm. Thus the theoretical distribution leads to the straight line

$$\log_{10} N_\xi = 4.0058 - 0.01388\xi. \tag{3}$$

This line is plotted together with the experimental points in Fig. 1. In Fig. 2 values of $\log_{10} n_x$ are plotted (A).

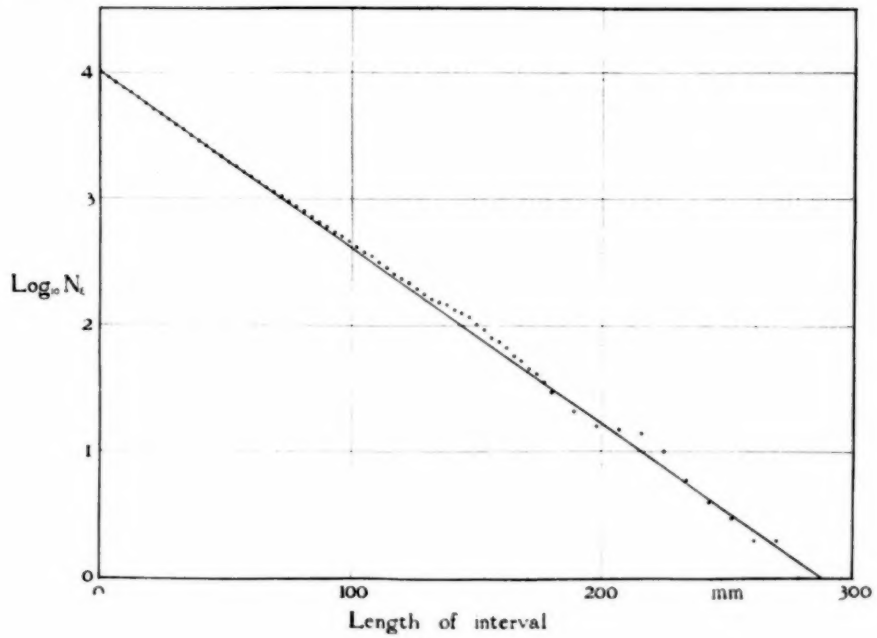

Fig. 1.

To a first approximation

$$n_x = -3(dN_\xi/d\xi)_x. \tag{4}$$

If this relation were strictly correct it is obvious from (1) that the graph of $\log_{10} n_x$ would be a straight line of the same slope as (3). A simple calculation shows that in fact a small correcting term ϵ is involved, depending on the ratio of the "plotting interval" (in this case 3 mm) to the mean length ω (here 31.28 mm), in such a way that

$$n_x = -3(1+\epsilon)(dN_\xi/d\xi)_x. \tag{5}$$

The condition of parallelism therefore remains, but the line as a whole is shifted slightly. Introducing numerical values we have

$$\log_{10} n_x = 2.9875 - 0.01388x. \tag{6}$$

This line is included in Fig. 2 for comparison with the experimental results. The straight line B, Fig. 2, corresponds to a plotting interval of 30 mm. Its equation, deduced in like manner to the above, is

$$\log_{10} \nu_x = 4.0039 - 0.01388x. \tag{7}$$

The corresponding points have been obtained by grouping the values of n_x in sets of ten—and the results are presented in this form, also, chiefly in order that they may be more nearly comparable with those of Kutzner, already referred to.

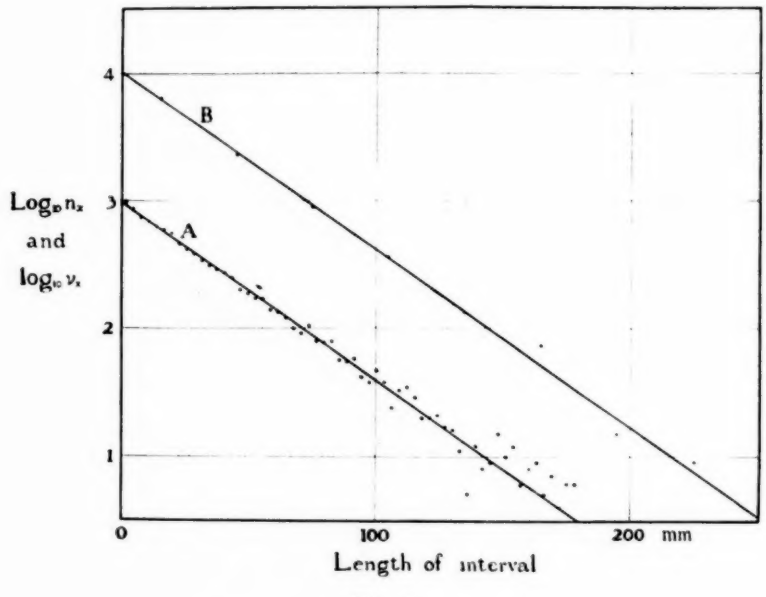

Fig. 2.

Discussion

Any consideration of the results here set forth must be twofold in character: there is the comparison of experiment with theory and, in addition, that of the present experimental results with those of previous investigators. But, before either comparison is made, it is necessary to consider what corrections, if any, should be applied to the crude observational material which the experiment provides—for the points plotted in Figs. 1 and 2 have been deduced without any corrections at all from the measurements of length on the chronograph record. First there is the varying activity of the source, which is entirely apart from any question of imperfection in the methods of registration. Depending upon the extent of this variation the theoretical logarithmic plot will depart more or less from the ideal straight line. At the time of the observations the strength of the source was in-

creasing daily by about 0.205 percent. Columns 1 and 2 of the accompanying table show how observations were spread over the thirty sessions on the thirteen days during which the experiment was in progress. They indicate that the mean interval ω, deduced from the full material, corresponds most probably to the true mean interval on the eighth day. Column 4 gives the true mean interval corresponding to each successive day calculated on this basis and column 3 the observed mean values obtained from the daily observations. Column 5 will be referred to at a later stage in the discussion. With the material which the table provides we may proceed to calculate the theoretical form of $\log_{10} N_\xi$ in the present experiments, which in the ideal case of the constant source was represented by Eq. (3). For each day's results the theoretical distribution is calculated from Eq. (1) using the

TABLE I.

1	2	3	4	5	1	2	3	4	5
Day	Number of intervals	Mean interval mm	True mean interval mm	Probable error mm	Day	Number of intervals	Mean interval mm	True mean interval mm	Probable error mm
1	381	31.7	31.73	1.6	8	373	30.2	31.28	1.6
						268	31.9		1.9
2	274	33.1	31.66	2.0		410	28.8		1.4*
	298	30.1		1.7					
					9	389	31.7	31.22	1.6
3	332	30.8	31.60	1.7		392	31.5		1.6
	191	32.5		2.4		428	29.4		1.4*
	261	32.6		2.0					
					10	452	27.5	31.15	1.3*
4	282	33.2	31.54	2.0		438	30.9		1.5
	212	31.2		2.1		407	31.1		1.5
5	104	27.9	31.47	2.7*	11	431	32.4	31.09	1.6
	137	39.5		3.4*		405	33.0		1.6*
	159	36.6		2.9*		421	31.1		1.5
6	352	30.4	31.41	1.6	12	469	29.2	31.02	1.3*
						439	29.7		1.4
7	347	33.8	31.34	1.8*					
	309	35.1		2.0*	13	431	30.4	30.96	1.5
	342	31.6		1.7					

appropriate value of ω. The individual distributions are then combined. When this somewhat laborious procedure was carried through it became evident that the greatest departure from the straight line of Eq. (3) was so slight as not to be appreciable on a diagram drawn to the scale of Fig. 1.

The second correction concerns the failure of the method of registration when scintillations succeed one another in rapid succession. It is not that scintillations are missed, but the actual time intervals are distorted on the record obtained. The first point in Fig. 2 (A) has reference to intervals of apparent length less than 3 mm (i.e. intervals shorter than 0.32 sec.): 988 measured intervals were distributed as follows; 0–1 mm, 0; 1–2 mm, 404; 2–3 mm, 584. Assuming, to a first approximation, that the number 988 is the true number of intervals in the three sub-groups in question we should expect a distribution giving 0–1 mm, 340; 1–2 mm, 329; 2–3 mm, 319 inter-

vals, respectively. Thus errors of registration have resulted in an apparent increase of length in the shortest intervals, and this must necessarily have been counterbalanced by an apparent decrease amongst the remainder. The figures quoted do not allow us to make any definite statement about the errors actually committed. At the one extreme is the supposition that in no case has the error been greater than 1 mm. On this basis we should assume that 340 intervals actually between 0 and 1 mm were recorded as between 1 and 2 mm in length, whilst 265 actually between 1 and 2 mm were recorded as between 2 and 3 mm long. At the other extreme is the supposition that all the intervals in the second and third groups in reality were correctly registered, the error lying entirely with the intervals of the first group. Then 75 members of that group could have been wrongly assigned to the second group and the remaining 265 members to the third. From the first point of view, amongst the total number of 10134 measured intervals (including the 988 shortest intervals with their newly assigned lengths) the correction of 605 1 mm errors of underestimation is necessary to rectify the crude distribution: from the second point of view the correction of 75 1 mm and 265 2 mm errors of underestimation is required. On account of the small fractions of the total which these numbers represent the two methods of correction lead to almost identical results. The former transfers 18.9 intervals from $n_{1.5}$ (originally 988), the second 19.4 intervals; these are effectively distributed amongst the various values n_x in gradually decreasing shares as x increases; thus $n_{4.5}$ is increased by 2.9, $n_{7.5}$ by 2.3 intervals, and so on. In Fig. 2(A) the change in position of the first point only is appreciable, as the figure indicates—and obviously to carry this correction to a further approximation is unnecessary.

From the above considerations, therefore, we may conclude that the experimental points of Figs. 1 and 2 and the straight lines accompanying them are entirely comparable: agreement between experiment and theory is to be measured by the closeness of fit of the points and the corresponding straight lines.

It must be admitted at the outset that the fit is good, though hardly as good as in the experiments of Curie.[5] On the other hand, by comparison with the results of Kutzner,[4] it will be seen that no such systematic deviations as he observed are in evidence here. It was not to be expected that they should be, since the concentration of active material in the source was smaller than the least concentration which Kutzner employed. Fig. 2 (B)—closely comparable with Figs. 2 (b), 3 (b) and 4 (b) in his paper—shows excellent agreement for the first five points and a non-systematic deviation later. Kutzner's figures likewise have five points closely on the theoretical straight line but, for his two stronger sources at least, the sixth and seventh points lie progressively below the line. Finally, making comparison with Pokrowski's results,[6] it is evident that no deviation of the order of magnitude of that reported by him is here present, though such deviation as there is in the earlier portion of Fig. 1 is certainly in the same sense as that which he observed. But the order of magnitude is entirely different. It is true that

in the present experiments the surface activity of the source was roughly twenty times as great as in the experiments of Pokrowski, but it must be emphasised that this is a macroscopic comparison. When the phenomenon of aggregation is taken into account it is obvious, for instance, that the size of the mean aggregate does not increase as rapidly as does the mean surface density of deposit during a single activation process, since new centers of aggregation presumably appear continuously throughout the process. Now it is unquestionably the size of the aggregates which is of importance for theories of the mutual action of neighboring atoms. Moreover it is almost impossible to make any *a priori* statement concerning aggregation when the mode of activation is different in the two cases to be compared.

It was pointed out earlier in the discussion that variations in the activity of the source, if sufficiently great, would lead to deviations from the theoretical distribution of the type of which Fig. 1 offers very slight indication and Pokrowski's results very marked evidence indeed. It has already been demonstrated that such changes cannot account for a non-linear relation in the present experiments, but it must be borne in mind that the same effect would be shown with a constant source and a varying efficiency of registration. It is very probable that this explanation is likewise inadequate. Column 5 of Table I gives the probable error in the thirty observed values of the mean interval and asterisks mark those cases in which the latter value differs from the true value (column 4) by more than the probable error. It will be seen that there are ten such cases as against twenty cases of closer agreement than that which the limits of probable error represent. Thus we are dealing with a set of observations more than normally uniform, and it is therefore unlikely that variations in registration efficiency are here in point.

Finally, in order to make sure that simple errors in length measurement were not vitiating the results, the total period of observation was deduced in two ways; first by adding together the measured lengths of the 334 periods, secondly by adding together the measured lengths of the 10134 intervals. In the latter addition the supposition was made that each interval classed as between x and $x+1$ mm in length was actually $x+0.5$ mm long. The first addition led to the value 316988 mm, the second to 317032 mm—a difference of one part in 7200. Moreover, the second sum would be expected to be slightly the larger of the two on account of the simplifying assumption introduced.

A Further Experiment—The Effect of Intense γ Radiation

In the account already referred to Pokrowski[6] has described a very remarkable experiment in which the irradiation of a weak source of radioactive material with γ-rays was found to produce an increase of 45 percent in the frequency of the scintillations observed. X-ray irradiation was reported to produce a similar effect. It was suggested that the possibility of such an effect was intimately connected with the use of a very weak source, in which the hypothetical mutual action of neighboring atoms was too small to be

effective. From this point of view the null result of earlier experiments with stronger sources was obviously explicable.[12]

There should, of course, be an intermediate case with sources a little stronger than Pokrowski's. The writer has carried out the analogous experiment employing a somewhat more concentrated source. To this end the arrangement of the previous investigation was modified in certain particulars; for instance it was no longer thought necessary to employ the maximum possible solid angle and it was recognised that it would be a great convenience to be able to remove the source from time to time. The latter was therefore carried on a rectangular glass plate (a fragment of the original gold leaf was attached to the smooth surface by means of a very thin film of castor oil) which when placed in its holder was maintained in a perfectly definite position, about 1.5 mm distant from the zinc sulphide screen. An area of about 2 mm^2 of screen was under observation. In the new arrangement the field illumination resulted in the screen being dimly lighted and the rest of the field relatively dark. This is an advantage, for, under sufficiently intense γ-ray irradiation, the screen becomes self-luminous and it is advisable to make conditions in the control experiment as nearly equivalent as possible.

The first comparison was made with a radon tube containing about 25 equivalent milligrams of emanation[13] placed on the axis of the system about

TABLE II.

1 mg	2	3 mm	4 mm	5
22.2	677	9.05	10.30	565
18.6	667	9.07	10.00	585
16.4	758	8.75	10.79	551
13.5	774	8.31	9.82	654
11.3	742	8.98	9.60	679
9.5	750	8.56	8.97	679
7.9	745	8.76	9.55	698
5.5	766	8.65	9.75	672
4.6	830	8.06	8.91	790
3.8	780	9.13	8.62	720
3.2	783	8.37	9.37	728
2.7	811	8.53	8.57	802
2.3	849	8.16	8.27	898
1.9	816	8.93	8.64	784
Totals	10748			9805

[12] When the present account was in the final stages of preparation Pokrowski's second paper (Zeits. f. Physik **59,** 427 (1930)) appeared in this country. In it a more detailed point of view is adopted and experimental data, obtained with a source of radium together with its subsequent products, put forward in its support. However, the experiments newly described differ in essential particulars from those of the writer, so that there is at present no basis of comparison. Nevertheless it may be remarked that if, as Pokrowski assumes, this process of induction is "saturated" in the ordinary case of a concentrated source, and if the mechanism is similar to that which he suggests, then the α-particles from such a source would not be homogeneous in velocity, but a distribution of velocities greater than the normal would also be present.

[13] The writer desires to thank Dr. C. F. Burnam of the Kelly Hospital, Baltimore, for providing him with this material.

3.7 cm distant from the source. The mean length of 1240 intervals recorded with the tube in position was 9.18 mm, 1181 intervals recorded when the tube was removed gave 9.33 mm. Within the probable error of the measurements, therefore, no difference was found. With this arrangement, however, the β and γ-ray luminosity of the screen was almost inappreciable and a further comparison was determined upon with more intense irradiation. The γ-ray tube was moved up in contact with the glass plate supporting the source.[14] Under these conditions the zinc sulphide screen fluoresced brightly and observations with the γ-ray tube in position[15] invariably led to greater values of the mean interval than those carried out when the tube had been removed. It was obvious that scintillations were being missed under the former conditions of observation. Table III summarises the comparisons made on successive days as the activity of the γ-ray tube decayed. A constant geometrical arrangement was used throughout. The strength of the γ-ray source is given in column 1. Columns 2 and 5 show the numbers of intervals

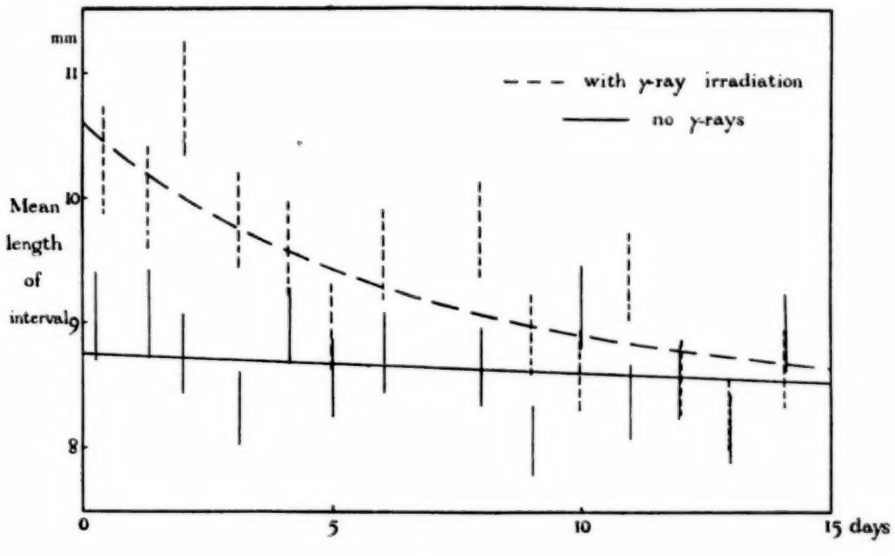

Fig. 3.

measured, in the first case with the γ-ray tube removed, in the second case with the tube in position. Columns 3 and 4 give the values of the mean interval deduced from these measurements. When the γ-ray activity had fallen to 4.6 equivalent milligrams the brightness of fluorescence which it caused was roughly the same[16] as the brightness of artificial illumination employed when the tube was absent; thereafter the very weak fluorescence with the tube in position was supplemented by a certain amount of artificial illumina-

[14] The thickness of the plate was 1.8 mm. The radon tube was contained in a brass case about 0.7 mm thick.

[15] The polonium source was exposed to the γ-rays only during the periods of observation, amounting to about half an hour daily.

[16] This comparison is necessarily inaccurate on account of the difference in quality of the light in the two cases.

tion also. In Fig. 3 the results are shown graphically. The lengths of the vertical lines indicate the magnitude of the probable error in each case. The gradual increase in the α-particle activity of the source during the period of the observations is clearly evident from the decrease in the mean interval determined with the source alone.[17] The broken line, which represents sufficiently well the trend of the apparent activity of the source under γ-ray irradiation, has been drawn in such a way that the difference between corresponding ordinates on this and on the full line, respectively, decreases according to the same law as the activity of the radon tube employed as the source of γ-rays. Whilst no great emphasis is laid on this way of exhibiting the results,[18] it does show at least that, as long as the effect is relatively slight the percentage of scintillations missed when observations are carried out in the presence of intense γ radiation is roughly proportional to the strength of that radiation.

Throughout the present experiments the observed effect of the irradiation of the source has been an apparent decrease in its α-particle activity. It was thought possible, however, that over a short period, during the decay of the γ-ray source employed, an apparent increase would be found. This might have been expected when the intensity of the residual primary β-particles and the secondary electrons produced by the γ-rays was just of the right order of magnitude to give rise to the type of multiple-β-particle scintillations described by Chariton and Lea.[19] Probably the requisite β-particle intensity was reached sometime between the tenth and the fifteenth day, but it is very doubtful indeed whether any trace of this phenomenon has been observed in the present case. Chariton and Lea, observing with a microscope of numerical aperture 0.65, classify this type of scintillation as very faint: it seems likely therefore that, observed with a less powerful microscope, they would only be recorded occasionally when α-particle scintillations were present as well.

In conclusion, therefore, it may be said that no effect has been observed which can in any way be attributed to the induction of disintegration in the polonium nucleus by any of the γ-rays of radium B+C. Very obviously this statement refers only to the concentration of source here employed, but it is interesting to remark that supposing a 10 percent effect had been observed at the beginning of the experiment, when the γ-ray source was most intense, then that would have corresponded to a reaction with the nucleus more than a million times more probable than the recognised types of reaction with the extra-nuclear electrons—and, moreover, this calculation is based on the supposition that γ-rays of all wave-lengths are capable of producing the nuclear change. The factor would be even greater if a selective effect were involved.

[17] In most cases observations with the source alone were carried out immediately after those under conditions of γ-ray irradiation. Occasionally this order was reversed, as may be seen from the figure, but without any systematic difference appearing.

[18] It may be remarked, for comparison with the earlier discussion, that of the 14 points belonging to each curve in Fig. 3, in each case 9 fall within the limits of probable error and 5 fall outside those limits.

[19] Chariton and Lea, Proc. Roy. Soc. **122A,** 335 (1929).

THE L SERIES SPECTRA OF THE ELEMENTS FROM CALCIUM TO ZINC

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Abstract

Using the first inside order of a plane grating (600 lines per millimeter) L lines of the elements Zn, Cu, Ni, Co, Fe, Mn, Cr, V, Ti and Ca have been measured. Separation of the $L\alpha$ and $L\beta$ lines as well as the L_l and L_η is attained by adjusting the grating so that the angle between the inside order and the plane of the grating is small. Under this condition the angular dispersion is given by $(d\alpha/d\lambda)=(1/D\beta)$, where D is the grating space and β the small angle between the plane of the grating and the first inside order. The results obtained are somewhat higher than those obtained by crystal measurements but are entirely consistent with the work of other experimenters. The failure of the $L\alpha$ and the $L\beta$ lines to appear in the case of calcium is in accord with Foote's extension of Stoner's arrangement of the electrons. All measurements are absolute.

THE study and measurement of x-rays of long wave-length have been handicapped by the extensive absorption in air of the rays and by the lack of satisfactory gratings, the grating spaces of ordinary crystals being much too small. The former difficulty has been overcome by the use of vacuum spectrographs; the latter to a certain extent by the use of organic crystals of large grating space. Extensive measurements of L lines in this region have been made by Thoraeus.[1] His work was done with a vacuum spectrograph using crystals of lauric acid ($2d=54.536$A) and palmitic acid ($2d=70.98$A). The wave-lengths given in his report are based on the sodium K_α line (11.884A). Shearer[2] has measured the nickel L_α line using the 100 face of a crystal of cane sugar ($2d=21.1519$A). Unfortunately, however, absorption in the crystal causes a considerable broadening of the spectral lines. It is also quite conceivable that the index of refraction might take on anomalous values due to a resonance frequency of the electrons in the crystal being near the frequency of the x-rays. Under these conditions the application of Bragg's law becomes uncertain even in its corrected form. For these reasons it seems advisable to apply the recently developed method of measuring x-ray wave-lengths from spectra obtained by reflection from a ruled grating to the study of the L lines under discussion.

When Professor A. H. Compton[3] showed in 1923 that x-rays could be reflected from plane surfaces at grazing angles smaller than a certain critical angle determined by the index of refraction of the x-rays reflected, he opened

[1] R. Thoraeus, Phil. Mag. **1,** 312 (1926); Phil. Mag. **2,** 1007 (1926).
[2] J. Shearer, Phil. Mag. **4,** 745 (1927).
[3] A. H. Compton, Phil. Mag. **45,** 1121 (1923).

up the possibility of using a ruled surface as a grating. Two years later Compton and Doan[4] obtained x-ray spectra from a ruled reflection grating. In 1926 and 1927 Thibaud,[5] Osgood,[6] and Hunt[7] applied the ruled grating to the study of the spectral region between x-rays and the ultra-violet, Osgood using a concave grating with a Rowland mounting. Since then the grating has been used by a number of investigators[8] in this field, some making the wave-length determinations from the constants of the apparatus, others by comparison with lines of known wave-length. This method has been used[9] to compare wave-lengths as measured by crystals with those measured by gratings. The measurements from gratings, using the constants of the apparatus, have been found slightly greater than the crystal measurements.

The general method used in the spectroscopy of soft x-rays has been reviewed by Osgood.[10] The general methods and results of this experiment were briefly presented by the author[11] to the American Physical Society. Kellström[12] has reported on measurements of the lines in this same region using outside orders of the spectral lines, comparing them with the K_α line of aluminum.

Theory of the Experiment

In making wave-length measurements in the optical region using a plane reflection grating the formula $n\lambda = D(\sin\phi - \sin\phi')$ is used, n being the order observed, λ the wave-length in centimeters, D the grating space in centimeters, ϕ the angle of incidence and ϕ' the angle of diffraction. In using the plane grating for measurements in the x-ray region it is more convenient to express the wave-length in terms of the grazing angle of incidence θ and the grazing angle of diffraction $\theta \pm \alpha$, the negative sign referring to inside orders, in which case,

$$n\lambda = D[\cos\theta - \cos(\theta \pm \alpha)]. \tag{1}$$

By a simple trigonometric transformation this becomes

$$n\lambda = 2D \sin\frac{2\theta \pm \alpha}{2} \sin\frac{\alpha}{2}. \tag{2}$$

[4] A. H. Compton and R. L. Doan, Proc. Nat. Acad. Sci. **11,** 598 (1925).

[5] J. Thibaud, Comptes Rendus **182,** 55 (1926); Comptes Rendus **185,** 62 (1927); Journ. Op. Soc. **17,** 145 (1928).

[6] T. H. Osgood, Phys. Rev. **30,** 567 (1927); Dissertation, Chicago (1927).

[7] F. L. Hunt, Phys. Rev. **30,** 227 (1927).

[8] B. B. Weatherby, Phys. Rev. **32,** 707 (1928). E. Bäcklin, Inaugurald Dissertation, Uppsala Universitets Arsskrift (1928). M. Söderman, Zeits. f. Physik **52,** 795 (1929). C. E. Howe, Proc. Nat. Acad. Sci. **15,** 251 (1929).

[9] C. P. R. Wadlund, Phys. Rev. **32,** 841 (1928); J. A. Bearden, Proc. Nat. Acad. Sci. **15,** 528 (1929).

[10] T. H. Osgood, Phys. Rev. Supp. **1,** 228 (1929).

[11] C. E. Howe, Phys. Rev. **33,** 1088 (1929).

[12] G. Kellström, Zeits. f. Physik **58,** 511 (1929).

Reference to Fig. 1 will help to visualize these angles. The beam of x-rays collimated by the slits, falls on the grating. The zero order is reflected to the point R, the first outside order to the point O and the first inside order to the point I. P is in the extended plane of the grating, while D is the position of the direct beam when the grating is removed.

It should be noted that the position of the inside order is farther removed from the zero order than is that of the first outside order, indicating greater angular dispersion for the inside order. Differentiating Eq. (1) with respect

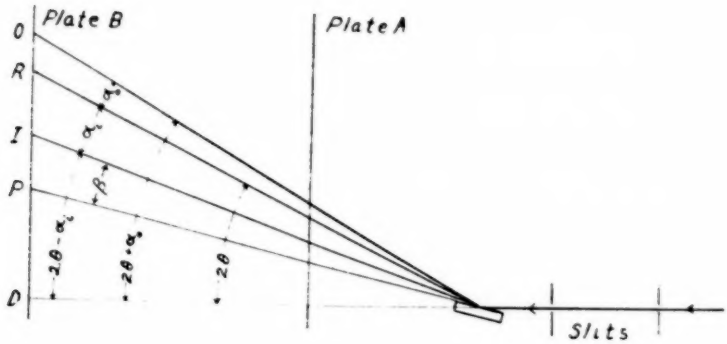


Fig. 1.

to α there is obtained the expression $n(d\lambda/d\alpha) = D \sin(\theta \pm \alpha)$where, as before, the plus sign refers to outside orders and the minus sign to inside orders. The angular dispersion may be written as

$$\frac{d\alpha}{d\lambda} = \frac{n}{D} \frac{1}{\sin(\theta \pm \alpha)} .$$

It is thus seen that the dispersion is greater for inside orders than for outside orders. By varying θ the position I of the inside order may be made as close as desired to the extended plane of the grating. In this way the angle $\theta - \alpha$, which we shall call β, can be made very small, resulting in a large dispersion. For the first inside order

$$\frac{d\alpha}{d\lambda} = \frac{1}{D\beta} . \tag{3}$$

Experimentally it has been found that there is a practical lower limit to the value of β; otherwise the dispersion could be made greater without limit as the angle β decreases. It is of interest to note that the dispersion is independent of both λ and θ.

For outside orders the theoretical maximum dispersion is obtained when $\sin(\theta+\alpha)$ is a minimum. This is the case when $\theta = 0$. The dispersion for outside orders then becomes (neglecting higher powers of $n\lambda/D$)

$$\frac{d\alpha}{d\lambda}=\frac{1}{D}\left(\frac{D}{2\lambda}\right)^{1/2}n^{1/2}.$$

If r represents the ratio between the dispersion of the first inside order and that of the maximum theoretical value of the nth outside order, then

$$r=\frac{1}{\beta}\left(\frac{2\lambda}{D}\right)^{1/2}\frac{1}{n^{1/2}}.$$

Actually the ratio will be larger than this since it is not possible to make $\theta=0$. In some cases in this experiment the dispersion obtained with the first inside order was equal to twelve times the theoretical maximum for the first outside order. To obtain the same dispersion in an outside order would require going to the 150th order.

The X-ray Spectrograph

Fig. 2 shows a horizontal cross section of the spectrograph and x-ray tube. The body of the spectrograph consisted of a brass tube 8 inches in diameter and 40 inches long. To one end-plate was attached the water-

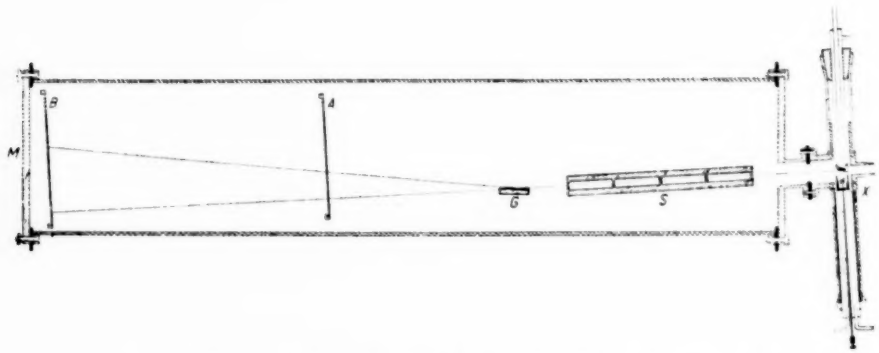


Fig. 2. Horizontal cross-section of the spectrograph and x-ray tube.

cooled metal x-ray tube X. The targets used consisted of small slabs of metal dove-tailed into the face of a water-cooled copper support. The tungsten filament was supported in the center of a water-cooled iron focusing cup.

To the same end-plate was attached a bed-plate on which the slit system, grating support, plate holders etc. were fastened. In order to collimate the rays and to exclude as much of the light from the incandescent tungsten filament as possible, the slit system S consisted of five slits. The two end slits, separated by a distance of 18 centimeters, were 0.05 mm wide; the three intermediate ones, 0.10 mm. By the passage through these slits the intensity of the light was so greatly diminished that it gave little difficulty. No trouble was experienced in the alignment of the slits in as much as the system consisted of two halves, half of each of the several slits being care-

fully machined into each metal piece, the two separate pieces then being clamped together.

The glass grating G, ruled 600 lines per millimeter, was mounted on a table which could be turned through any desired angle by means of a train of gears controlled from the rear end of the spectrograph near the end-plate M. This table, in turn, was mounted on a slide so that the grating could be removed from the path of the x-rays, this movement also being controlled from the rear end. The mechanism was so constructed that either operation could be performed without disturbing the setting of the other, and also so that definite settings could be reestablished with sufficient accuracy.

The plate holder A served to hold a plate which intercepted the lower half of the radiation coming from the grating. The upper half was recorded on a plate placed in the holder B. Plate A was made perpendicular to the direct beam as follows. One side of the slit system was removed, and a straight iron bar carefully clamped to the other half. With a precision square, A was made perpendicular to the bar within a few minutes of arc. B was then made parallel to A by means of an inside micrometer, this operation serving also to obtain the distance between the two plate holders. This distance was 37.982 cm.

All of the apparatus described thus far was mounted as one unit. It could be removed from the main body of the spectrograph at any time for purposes of adjustment.

After adjustment this unit was placed in the spectrograph, a sulphur-free rubber gasket being placed between the end-plate and the body. Plates (Eastman process) were put in holders A and B, and the spectrograph evacuated to a pressure of about 2×10^{-4} mm. A pressure considerably lower than this was maintained in the x-ray tube by means of a separate set of mercury vapor pumps. An exposure of from one to twelve hours was made, depending on the intensity of the radiation. After about twenty minutes exposure the reflected beam was covered with a small screen (operated by an electromagnet) to prevent over exposure and fogging. The exposure being completed, air was admitted, the end-plate M taken off and the grating removed from the path of the beam. After reevacuation the direct beam was exposed for a minute or two.

A small vessel containing phosphorus pentoxide was kept inside the spectrograph to absorb water vapor. The life of the tungsten filament was increased greatly by having a liquid air trap close to the x-ray tube to take up moisture.

The current through the x-ray tube varied from 15 to 40 milliamperes. Because a transformer having rather high secondary resistance was used it was not practicable to attempt to measure the effective voltage on the target, which was much lower than the inverse voltage across the self rectifying tube. It may be estimated that the effective voltage varied from 4000 to 12000 volts.

The Spectra

Fig. 3 shows typical spectra obtained. These particular spectrograms, having nearly equal values of θ, were selected to show the relative displacement of corresponding lines and the increased dispersion with smaller values of β. The L_α and L_β lines of zinc are not resolved. The corresponding lines

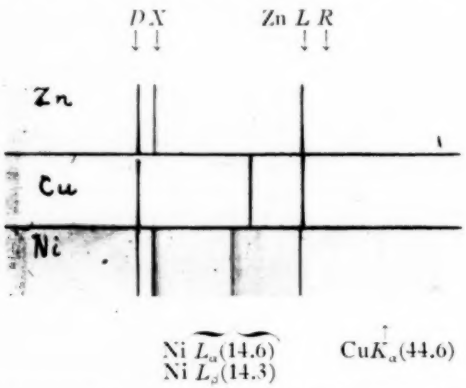
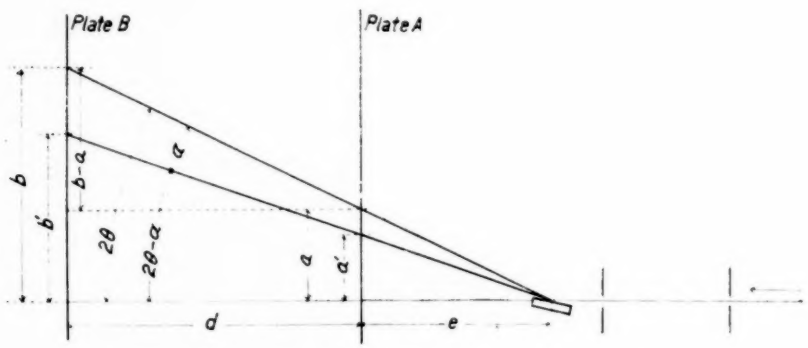


Fig. 3. Typical L series spectra of Zn, Cu and Ni. D is the direct beam, R the reflected beam and X is light diffracted past edge of grating.

of copper overlap, the more intense L_α line being to the left. The lines of nickel are resolved. Since about the same wave-length difference exists between these lines, the spectra show the increase in dispersion as the inside order approaches the plane of the grating. Of the three spectrograms shown only that of nickel is useful in making measurements on the L_β line.



$$\tan 2\theta = \frac{a}{e} \text{ or } \frac{b}{d+e}, \quad \tan (2\theta - \alpha) = \frac{a'}{e} \text{ or } \frac{b'}{d+e}, \quad e = \frac{a}{b-a} d.$$

Fig. 4.

It was found that the first inside order from the grating used was much greater in intensity than the outside orders. This fact, combined with the great dispersion obtained with inside orders, contributed greatly to the success of the work. It was also found that the intensity of the L radiation from

the elements studied depended greatly upon the operating conditions of the tube. It was most intense when the temperature of the focal spot was maintained very close to the melting point. With this condition the spot was kept very clean.

The measurement of the plates and the calculation of results can best be described with reference to Fig. 4. The size of the ruled surface (2 cm×2 cm), the width of the x-ray beam (approx. 0.1 mm) and the magnitude of the grazing angle (more than 2°25′) make it possible to have the entire beam "reflected" from the ruled surface of the grating. Hence all measurements may be made to the centers of the recorded lines. The positions of the lines on the plates were taken as a mean of at least ten independent settings on a Gaertner comparator. The probable error in the readings was usually less than 0.003 mm. The distance e of plate A from the grating and the angles 2θ and $2\theta-\alpha$ were obtained as indicated. By subtraction α was found and substitution made in Eq. (2) to obtain the wave-length.

The results of the measurements are shown in Table I, which gives both the wave-length in angstroms and the value of (ν/R).[1/2]

TABLE I.

Element		$L\alpha_{12}$		$L\beta$		Ll		$L\eta$	
		λ	$(\nu/R)^{\frac{1}{2}}$	λ	$(\nu/R)^{\frac{1}{2}}$	λ	$(\nu/R)^{\frac{1}{2}}$	λ	$(\nu/R)^{\frac{1}{2}}$
30	Zn	12.25	8.63	11.96	8.73	14.02	8.06		
29	Cu	13.37	8.26			15.33	7.71	14.95	7.81
28	Ni	14.62	7.90	14.28	8.00	16.73	7.38	16.36	7.47
27	Co	15.99	7.55	15.64	7.64	18.34	7.05		
26	Fe	17.66	7.18	17.29	7.26	20.25	6.71		
25	Mn	19.55	6.82	19.17	6.89	22.34	6.39		
24	Cr	21.73	6.48						
23	V	24.31	6.12			27.70	5.73		
22	Ti	27.48	5.76						
20	Ca					39.63	4.79		

DISCUSSION

Fig. 5 is a Moseley diagram of the results. The results here given are all higher than those obtained by Thoraeus[1] and Shearer.[2] This is in accord with the results obtained by other experimenters.[13] Kellström has reported measurements on most of these lines, using outside orders which did not permit the resolution of the α and β lines or of the l and η lines. His values for the α and l lines are less than those reported here. This is, of course, due in part to the added weight of the unresolved β and η lines. However, in the case of the β line at least, the relative intensity is so much smaller than that of the α line that the wave-length determined from the measurement of the unresolved lines is far from the mean of the two component wave-lengths. Comparison of the results of the two experiments is therefore limited. This is further complicated by the fact that Kellström has made his measurements by comparison with the K_α line of aluminum as obtained from crystal

[13] A. H. Compton, Jour. Franklin Inst. **208,** 605 (1929).

measurements. This would also make his measurements lower. In view of these considerations the agreement between the two experiments is very satisfactory, with the exception of the l line of calcium for which Kellström

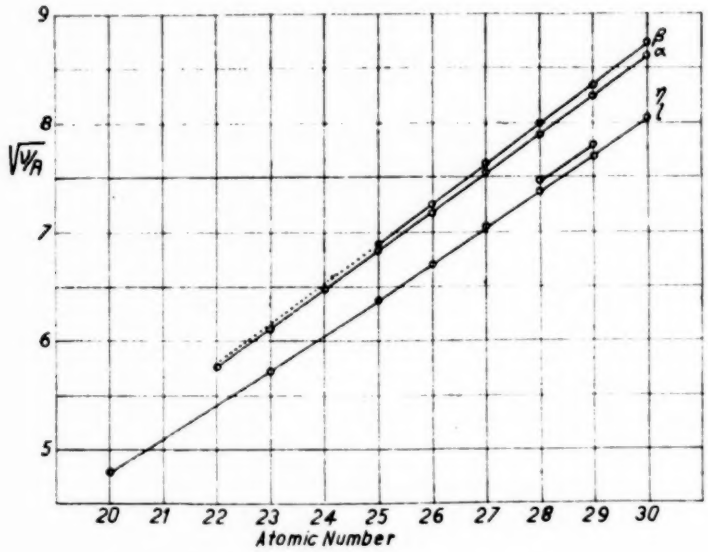


Fig. 5. Moseley diagram for L-series lines.

finds a value three percent higher than the value here given. Unfortunately the author recorded this line on but one plate and could not therefore check this wave-length carefully. In all but a few cases, however, sufficient values were obtained to give a probable error less than 0.01A.

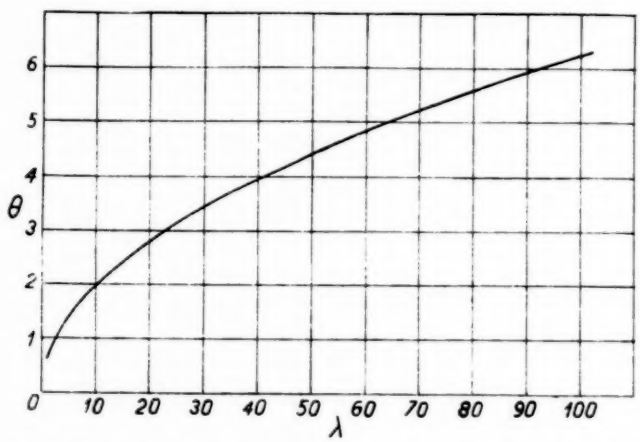


Fig. 6. Values of θ for which the inside order should be in the plane of the grating.

In order to resolve the α and β lines as well as the l and η lines it was necessary to rotate the grating so that the inside orders occurred close to the plane of the grating. Consequently each element required at least two

independent settings; one to resolve the α and β lines, the other to resolve the l and β lines. In order to facilitate this operation the angle θ was calculated for which the inside order should be in the plane of the grating. Fig. 6 shows this value of θ in degrees plotted against the corresponding value of λ in angstrom units. In actual practice θ was made a little larger than this critical value.

For most of the elements in this region the L_α line is really two lines, the $L\alpha_1(M_{33}-L_{22})$ and the $L\alpha_2(M_{32}-L_{22})$. According to Foote's extension of Stoner's arrangement of the electrons the M_{33} level disappears with vanadium and the M_3 level with calcium. This means that neither of the two components of the $L\alpha_{12}$ line should be observed for calcium. Reference to Fig. 1 shows that it was not observed in this experiment although Kellström[12] finds it present. The $L\beta_1(M_{32}-L_{21})$ line should also disappear with calcium.

In conclusion I wish to express my indebtedness to Professor A. H. Compton of the University of Chicago under whose direction the experimental work was done.

THE CYBOTACTIC (MOLECULAR GROUP) CONDITION IN LIQUIDS; THE NATURE OF THE ASSOCIATION OF OCTYL ALCOHOL MOLECULES

By G. W. Stewart
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(Received January 15, 1930)

Abstract

In resumè twelve experimental lines of evidence are cited in favor of the adoption of the molecular group theory of the nature of liquids. This theory is assumed in the interpretation of results with octyl alcohols.

The following twenty-two octyl alcohols were used: octanol −1, −2, −3, −4, 2-methyl heptanol −1, −2, −3, −4, 3-methyl heptanol −1, −2, −3, −4, 4-methyl heptanol −1, −2, −3, −4, 5-methyl heptanol −1, −2, −3, 6-methyl heptanol −1, −2, −3.

The value of the effective diameter of the primary normal alcohols is approximately 4.5 A. With these octyl alcohols the increase for OH and CH_3 in a branch is approximately 0.0 A and 0.24 to 0.75 A respectively. When attached to the same carbon atom the increase caused thereby is not noticeable. These results are in fair agreement with previous similar measurements of isomers with other primary alcohols.

Two types of association were found. When the OH group is attached to the end or next to the end of the alcohol molecule, two of these molecules are associated end to end, the lengths of the chains being in the same straight line. On the other hand when the OH group is attached to any other carbon atom, the molecules are associated side by side. This is shown by the planar distances in the direction of the molecule which indicate in the first case the length of two molecules and in the second case the length of a single molecule.

DURING the past four years evidence has been accumulating in favor of the view that in liquids in general there exist temporary, fairly orderly, not sharply defined molecular groups. A brief resumé of that evidence, as an introduction to the present experiments, is opportune. Skepticism concerning the correctness of this conception of molecular groups is natural, since it has formerly been accepted that the molecular motions in a liquid are somewhat independent. Moreover it is known that molecules of a gas, which are certainly not orderly, will give x-ray diffraction haloes.[1]

Evidence for the Cybotactic Condition

It will be the purpose of this statement of evidence to present the material merely in outline. The reader can easily follow the argument by studying the experimental results mentioned in each case. For the sake of simplicity the references will be limited but the articles to which references are made contain the complete bibliography. It is believed that the evidence establishes the group theory as one worthy of confidence. The chief points will be now enumerated. All the experiments refer to x-ray diffraction.

[1] Debye, Phys. Zeits. **30,** 524 (1929); **31,** 142 (1930).

1. Scattering centers at randon would produce a large scattering near 0°, for in the terms of a wave theory, the nearer the approach to 0° the more nearly the agreement in phase. But crystals and crystal powders would, if ideal, give zero diffraction near but not at 0°. With them, interference would produce zero intensity excepting at angles of regular reflection.[2] Now it is found that in liquids, in general, we find the diffraction near zero to be similar to that of crystal powders and not to amorphous substances. The author and his co-workers[3] habitually approach zero diffracting angle to the limit permitted by the resolving power of the instrument, 24′, and they find the intensity small and decreasing as 0° is approached.

2. With normal monobasic fatty acids,[4] one diffraction peak alters its angular position with the number of carbon atoms in the chain in such a manner that the corresponding lengths (computed by Bragg's diffraction law) vary linearly with the carbon content. This is precisely what has been found[5] with the same fatty acids in solid form and the distances and rate of change are approximately the same in the solids and liquids. Similar causes are presumably operating in the two cases. If the solid is crystalline, the liquid has molecular groups.

3. Comparisons between the solid and liquid diffraction curves show a clear similarity. Of course the diffraction peaks are diffuse as compared with the lines with crystals. But the prominent maxima are similarly located. Krishnamurti[6] has published comparisons of eight substances. There have also been published lauryl alcohol[7] and capric acid[8] diffraction curves. Triphenylmethane shows a like result. The chief maxima of intensity occur apparently at nearly the same angles of diffraction.

4. Binary solutions, where the components are miscible, show not the diffraction intensity maxima of both components, but a modification as of a single liquid. This is analogous to the case of a solid solution,[9] and can readily be explained by the molecules of the solute participating in the molecular groups of the solvent. This is a reasonable picture of the nature of a solution.

5. The area occupied by the cross-section of a molecule of normal monobasic acids in a surface film on water[10] is the area as computed by measurements within such a liquid assuming the group theory.[11] It is also the area computed from similar measurements on primary n-alcohols.[12] The grouping

[2] Regular reflection occurring at a very small glancing angle less than the critical angle, need not be regarded here.

[3] See series of articles by Stewart, Stewart and Morrow, and Stewart and Skinner in Phys. Rev. 1927–29.

[4] Morrow, Phys. Rev. **31,** 10 (1928).

[5] See footnotes in Morrow, reference 4.

[6] Krishnamurti, Ind. Jour. Phys. III, II, 225 (1928).

[7] Stewart and Morrow, Phys. Rev. **30,** 232 (1927).

[8] Morrow, reference 4.

[9] Krishnamurti, Ind. Jour. Phys. III, III, 331 (1929); Hertlein, Zeits. f. Physik **54,** 341 (1929). Also unpublished results by A. W. Meyer of this laboratory.

[10] Adam, Proc. Roy. Soc. **99A,** 336 (1921); **101A**, 452, 456 (1922); **103A**, 676, 687 (1923).

[11] Morrow, reference 4.

[12] Stewart and Morrow, reference 7.

of the molecules in such a surface film is acknowledged. Similar dimensions obtained on the interior argues strongly for molecular groups.

6. The group theory leads to simultaneous measurements of two and occasionally three distances. These are in striking consistency and difficult of explanation otherwise. For example, the molecular "diameters" remain constant with increase in the length of the chain.[11,12] Again, di-n-propyl carbinol gives three distances,[13] of which two, 4.85 and 4.5 A.U., are consistent with the interpretation that the former is a measurement of the diameter in the direction of the branch and the latter the diameter of the chain perpendicular thereto, or the diameter of the primary n-alcohol.

7. Assuming the group theory, isomers of primary n-alcohols have been measured[12] and these have been found consistent with the usual chemical views as to structure.

8. The effect of temperature on the diffraction in liquids is, in general, similar to that in crystal powders, i.e., a shifting of the maxima to smaller angles, an increase in diffuseness and a decrease in intensity.[14]

9. There are two peaks with the primary n-alcohols[12] and only one with n-paraffins.[15] This is in harmony with the group theory. Each series has parallel chains, but the polar molecules produce a longitudinal orderly arrangement that makes possible the second spacing of diffraction centers as found by x-rays.

10. The relative magnitude of the two diffraction peaks in case of the n-alcohols and the saturated normal fatty acids indicate that the intensity obtained by the diffraction from the parallel planes containing the lengths of the chains is much greater than from the parallel planes passing across these chains. Consideration of the structure factor in these two cases shows that a relative magnitude of this order should be anticipated if the group interpretation is correct. The quantitative details of these considerations are not yet published.

11. Quantitatively the dimensions determined by some of the diffraction maxima are much too long to refer to parts of the same molecule and must refer to intermolecular spacing.

12. The integrated intensity in the region of the chief diffraction maximum for solid (powdered crystal) and liquid triphenylmethane (results unpublished), show approximately equal values. It is difficult to see how such coherence could be obtained from a liquid without groups.

These are the more conspicuous lines of argument. But even aside from the evidence, a moment's general consideration indicates the reasonableness of the cybotactic theory. For the molecular forces are evidenced in surface tension, where there is an orderly arrangement, and, with the closeness of approach of molecules in the liquid, these forces must everywhere be of importance. These force fields introduce potentials. From Boltzmann's statistical distribution law the largest number of molecules must be at the

[13] Stewart and Skinner, Phys. Rev. **31,** 1 (1928).

[14] Vaidyanathan, Ind. Jour. Phys, III, III, 391 (1929); E. W. Skinner, not yet published.

[15] Stewart, Phys. Rev. **31,** 174 (1928).

least potential. It is then merely a question as to what the possible potentials are. Will the least potential be an orderly periodic arrangement or not? *A priori*, one cannot say, but such considerations would cause one to be ready to adopt the answer favored by experiments. From this view point the above twelve items of evidence seem to lead to the adoption of the cybotactic conception as the best description of the condition of least potential.

X-ray Diffraction in Octyl Alcohols

The present contribution was made possible by Professor E. Emmet Reid of Johns Hopkins University who kindly lent samples of the twenty-

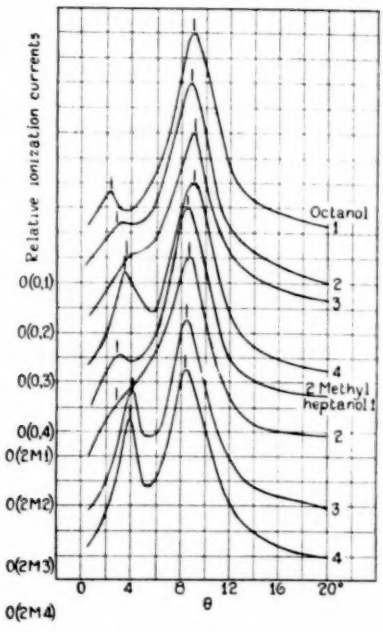

Fig. 1. X-ray diffraction; relative ionization currents of octyl alcohols.

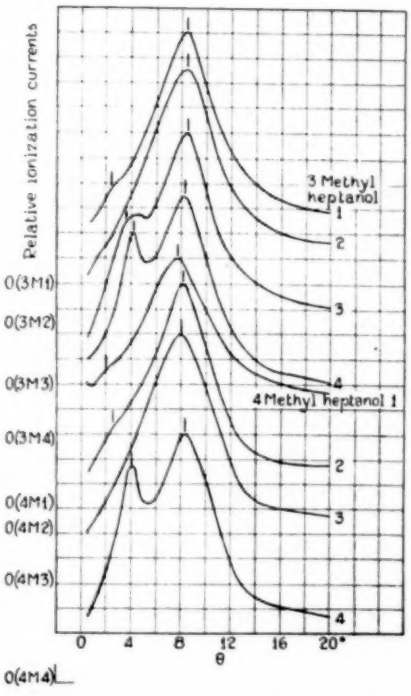

Fig. 2. X-ray diffraction; relative ionization currents of octyl alcohols.

two octyl alcohols made in his laboratory by Messrs. H. B. Glass and G. B. Malore. The following gives a statement of results and conclusions of x-ray diffraction measurements. The description of the apparatus and precautions may be found in one of the earlier articles.[16]

In Figs. 1, 2 and 3 are presented the relative ionization currents obtained in a chamber placed at the varying angles of diffraction. In each figure the curves are displaced vertically and each major peak is given the same magnitude. In Fig. 4 are shown the diameters and lengths of the molecules. Bragg's law of crystal diffraction, $\lambda = 2d \sin \theta/2$, wherein λ is the wave-length, d, the separation of planes containing diffraction centers and θ, the angle of dif-

[16] Stewart and Morrow, Phys. Rev. **30**, 232 (1927).

fraction, is used. The circle containing a cross is the length of the molecule estimated from the *n*-paraffin chain dimensions obtained in an earlier article.[17]

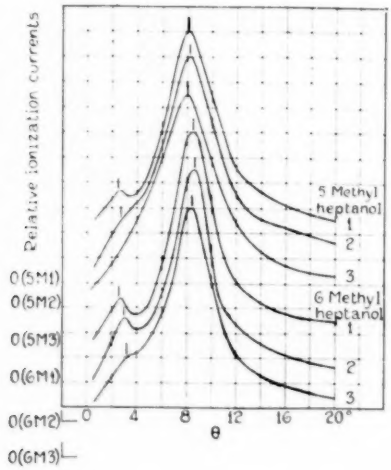

Fig. 3. X-ray diffraction; relative ionization currents of octyl alcohols.

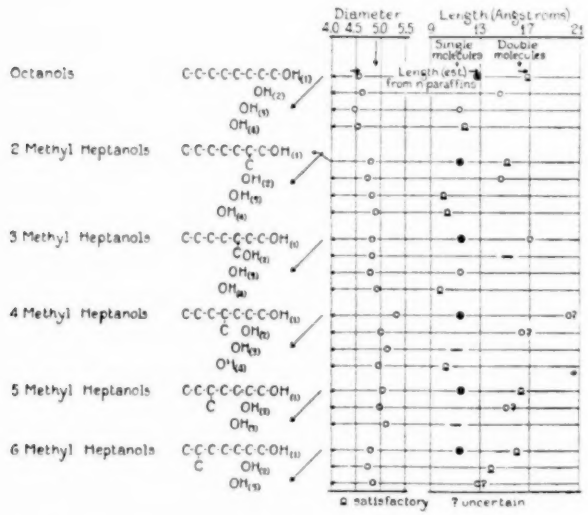

Fig. 4. Effective diameters and comparison of molecular lengths with separation of second set of diffraction planes.

Conclusions

1. *Molecular diameters.* The effective molecular diameter of octanol-1 is about 4.55×10^{-8} cm (or A.U., indicated merely by A, for the sake of brevity). This is more accurately the mean separation of planes containing parallel

[17] Stewart, Phys. Rev. **32,** 153 (1928). The length of a normal paraffin molecule is $1.24n+2.70$ where n is the number of carbons and 2.70 is the length estimated for the two terminal hydrogen atoms. The formula is used for the alcohol molecules, save that n does not include the carbon atom in a branch.

molecules and, assuming a square array of the chains in a plane perpendicular thereto, this distance may be interpreted as the effective molecular diameter. It is to be noted that (1) with the group OH in a branch the diameter is not materially increased, (2) with CH_3 in a branch the diameter is increased by approximately 0.24A for 2-methyl-, 3 methyl- and 6 methyl-heptanol 1, (3) by 0.75A for 4-methyl-heptanol and (4) by 0.47A for 5-methyl heptanol. Items (1), (3) and (4) are closely in accord with previous findings on isomers of primary n-alcohols,[18] but the increases noted in (2) are approximately one-half as great. Also, as before, the effect on the diameter of the attachment of OH and CH_3 to the same C atom is not noticeable. The measurements are not in error by more than 0.05A, but there are other factors to consider. For example the compounds are doubtless not of the highest practicable purity. Also, we are interpreting the grouping in the simplest possible manner, and this picture of the grouping may be only approximately true. Again, the position of the peak in the curve is a statistical result and is not obtained with a *fixed* grouping of molecules.

2. *Association of molecules.* As shown in earlier articles[19] the distance computed from the position of the smaller peak depends upon the length of the molecule but cannot represent the molecular length or an integral value of it because the association produces effective diffraction centers that lie in planes not perpendicular to the molecular lengths. For the primary normal alcohols and the saturated normal fatty acids the distance between the planes was more than the length of the molecule and less than twice this distance. The interpretation was made that two polar groups were associated so that their molecules were placed end to end in the same line. Consequently the effective longitudinal diffraction centers occurred every two molecules. But the planes containing them were not perpendicular to the molecules. Thus the planar distance became less than twice the length of a molecule. In Fig. 4 of this contribution it is noticed that the determination of all the secondary peaks was not possible. But of those obtained, the computed planar distances represented in Fig. 4 convey an interesting result. All the molecules having OH at the end of the molecule or attached to the second C atom, show a distance between planes considerably greater than the computed molecular length and yet clearly less than twice this length. On the other hand when OH is attached elsewhere, the planar distance is approximately the computed molecular length. We hence have here *two different types of association. When the polar group OH is at 1 or 2, the association arranges the molecules end to end in the same line with two polar groups adjoining. When the OH is elsewhere, the associated molecules lie side by side.* This generalization is further verified by the cases of diethyl carbinol and di-n-propylcarbinol.[20] The computed molecular length of the former, using the same figures for distance occupied by atoms as described above, is 8.9A, and the latter 11.38A, whereas the distances between planes are 8.9A and 10.5A, respectively. Considering the

[18] Stewart and Skinner, Phys. Rev. **31,** 1 (1928).

[19] Stewart and Morrow, reference 16 (for normal primary alcohols). Morrow, Phys. Rev. **31,** 10 (1928), (for saturated normal fatty acids).

[20] Stewart and Skinner, reference 18.

inaccuracy of the length computed from atomic dimensions in the molecule, this is clearly an agreement.

3. *Variation in magnitude of secondary peaks.* An interesting variation in relative heights of the secondary maxima can be seen in Figs. 1 to 3. This secondary diffraction peak is the most prominent in the cases of octanol-4, 2-methyl-heptanol-4, 3-methyl-heptanol-4, 4-methyl-heptanol-4; or, in other words, given the position of the methyl group, the secondary diffraction peak is always the greatest with the OH group on the fourth carbon atom. In fact, there is a variation in magnitude through any such set. These are significant facts but their interpretation is not altogether clear. In the first place one must expect the arrangement of atoms to affect the intensity of diffraction (through the much used structure factor, F). As to the major peak, the intensity of diffraction for all is sensibly the same. The experiments required the use of very thin cylindrical glass receptacles, one for each compound. Differences in these and in the sensitivity of the ionization chamber (which is refilled only once in several months), were not large and the results for the magnitude of the diffraction intensity at the major peaks, even including these unavoidable changes mentioned agreed for all the liquids with an average deviation of 17 percent and a maximum deviation from the mean of 30 percent. And this is what should be expected for the changes in structure of these molecules would result in but little change in the structure factor when the molecular length lies in the diffracting planes. Since, then, the magnitude of intensity of the major peaks is of the same order, comparison may be made of the secondary peaks as plotted in Figs. 1, 2, and 3, assuming the major peaks the same magnitude. The difference in secondary peaks is relatively very great. The structure factor for diffracting planes perpendicular to the molecular length, or at any considerable angle, would vary greatly also. Hence this may be in part the explanation of the experimental results. But the second possible explanation is that, although the molecules may lie with lengths parallel, and give well-marked diffraction planes containing these lengths, yet the molecules may not be so regularly arranged for the other set of planes mentioned. The space arrangement longitudinally may not be so perfect. One need not choose between these two factors, for both doubtless exist in important degrees. Computations are at present being made of the probable variation in structure factor, though of course there is much conjecture involved. As to the perfection of the grouping, there now appears some enlightenment through the study of the viscosity of these liquids. In fact, the viscosity is greatest where the secondary peak is greatest. This correlation is doubtless important and will be discussed in a future article by Dr. R. L. Edwards and the author. In the foregoing it must be understood that the cybotactic condition is not one in which the "groups" are definite, having constantly the same consituents, or the same dimensions or spacing. There must be groupings to give the diffraction effects at any instant, but the effect on the ionization chamber is a statistical one.

To Professor E. Emmet Reid for the use of the octyl alcohols and to Mr. H. A. Zahl, research assistant, who is responsible for the data described herein, I wish to express my thanks.

BARKHAUSEN EFFECT
II. DETERMINATION OF THE AVERAGE SIZE OF THE DISCONTINUITIES IN MAGNETIZATION

By Richard M. Bozorth and Joy F. Dillinger
Bell Telephone Laboratories, New York, N. Y.

(Received February 12, 1930)

Abstract

When the magnetic field-strength acting on a ferromagnetic material is changed, the magnetization changes discontinuously (Barkhausen effect). These discontinuous changes have been examined in 1 mm wires; an expression is derived and experimental arrangements are described for determining their average size for a given material in a given state of magnetization.

Experimental determinations of the average size have been made for iron (including a single crystal and a hard-drawn wire), nickel, and several iron-nickel alloys (permalloys). The average size is greatest on or near the steepest part of the hysteresis loop. The greatest average size, expressed as the volume of material the magnetization of which must be changed from saturation in one sense to saturation in the opposite sense to produce the same change in magnetization, is much the same for all of the materials examined, the extremes being 1.2×10^{-9} cm^3 for annealed iron and 45×10^{-9} cm^3 for 50 percent nickel permalloy. This shows that the sizes of the discontinuities do not depend to any considerable extent on the size or kind of crystals.

Criticism is made of previous work on the size of the coherence region, the region within which the change in magnetization is confined. Although the effect of a single discontinuity in magnetization may be detected as far as 10 cm from its source because of the eddy-currents induced, the experimental evidence is consistent with the view that the permanent change in magnetization is confined to the volume in terms of which the size of the discontinuity is measured as stated above, always less than 10^{-6} cm^3.

Introduction

IT IS a well-established fact that when a continuously-varying magnetic field is applied to a ferromagnetic substance, the induction varies not smoothly, but by sharp sudden jumps or "discontinuities." One may interpret it by supposing that the substance is made up of very small regions or "units," each of which is always magnetized to saturation, and that during the magnetization of the sample, the magnetic axes of half of these are reversed, one after another. The volume v of each unit may then be computed from the amount of the corresponding discontinuity. Of course, it may be that the change in the magnetic moment of a unit is less drastic than a complete reversal of all the atomic magnets; in that case, the value of v computed by our formula will be proportionately smaller than the actual volume of the region. However, it is simpler, and we believe also that for discontinuities on the steeper parts of the hysteresis loops it is correct, to interpret v in the first-mentioned manner.

We wish to know the average sizes of these units for as many ferromagnetic materials and as many parts of the magnetization curve as possible. Especially we wish to compare it with the sizes of the crystals on one hand, of the smallest magnetizable atom-groups on the other. For instance, one of us[1] has shown, for a variety of materials, that on the steeper parts of the hysteresis loop nearly all the discontinuities correspond to units larger than 10^{-13} cm^3, comprising more than 10^{10} atoms.

In the present work we have obtained data relevant to these questions by determining the average amount of the discontinuities on various segments of the hysteresis-loops of several substances: iron, nickel, several permalloys both annealed and hard-worked, and a single crystal of iron.

Theory

In our apparatus a slowly and uniformly changing magnetic field acts on the cylindrical specimen P, Fig. 1. When a sudden change, characteristic of the Barkhausen effect, occurs in the induction B in the sample, an e.m.f.

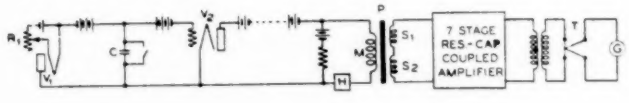

Fig. 1. Diagram of the apparatus.

is induced in one of the search coils S which are connected in series opposition to the input of an amplifier. At any instant the e.m.f. impressed on the amplifier is equal to the algebraic sum of the separate e.m.f.'s induced in the two coils. The e.m.f. in each coil is proportional to the dB/dt in the material inside of that coil, consequently when the coils are connected in opposition the e.m.f. acting on the amplier, and the output current, i, are proportional to the difference between the values of dB/dt within the two coils. Considering dB/dt in one coil to be positive and that in the other to be negative, the difference is $(dB/dt)_1+(dB/dt)_2$, and the mean value of this sum, or $\overline{dB/dt}$ for the combination, is zero. The thermocouple T measures $\overline{i^2}$ (the mean value of i^2) which is then proportional to $\overline{(dB/dt)^2}$. We can now use a statistical relation derived by T. C. Fry,[2] provided the following assumptions are valid:

(1) The law of superposition holds; that is, the e.m.f. impressed on the amplifier at any time is the algebraic sum of the separate e.m.f.'s induced by separate sudden changes in induction.

(2) The discontinuities are random in character both as to magnitude and time; that is, the magnitude and exact time of beginning of any sudden change in induction is independent of previous changes.

[1] R. M. Bozorth, Phys. Rev. **34,** 772–784 (1929). See also an abstract of the present paper, Phys. Rev. **33,** 1071 (1929).

[2] T. C. Fry, J. Frank. Inst. **199,** 203–220 (1925).

(3) The form of the induction-vs-time relation is the same for all the impulses produced by the various discontinuities; that is, any impulse is identical with the product of any other by some constant factor.

(4) The time required for the thermocouple reading to reach a steady value is large compared to the duration of a single current impulse but small compared to the gross changes in the output of the amplifier, corresponding to what may be considered changes in the magnetic state of the material.

These assumptions are valid except in relatively minor details. Assumption (2) is not exactly true unless the material inside one search coil has exactly the same magnetic characteristics as that inside the other. In reality materials are not quite homogeneous. Assumption (3) implies that the magnetization in a small volume changes very suddenly but that the e.mf. induced in the search coil is influenced by the rate of decay of the eddy-currents set up by the change in magnetization. If these small volumes are located at different distances from the axis of the sample, the eddy-currents will decay at slightly different rates and assumption (3) is not strictly correct.

The equation derived by Fry is

$$S = \bar{\nu}\bar{w}, \tag{1}$$

where S is the power expended in the thermocouple, $\bar{\nu}$ the mean number of separate impulses occurring per second, and $\bar{w}$ is the average energy expended in the thermocouple by a single impulse. Obviously,

$$S = \overline{i^2}R, \tag{2}$$

where R is the resistance of the thermocouple and $\overline{i^2}$ is the mean square current through it. The mean frequency of the impulses, $\bar{\nu}$, may be expressed in terms of the average volume of material, $\bar{v}$, the magnetization of which is assumed to change from saturation in one direction to saturation in the other:

$$dB/dt = 8\pi I_s \bar{v}\bar{\nu}/V, \tag{3}$$

where I_s is the saturation value of magnetization and V is the total volume of the sample in which magnetic discontinuities affect the search coils.[3] The energy w for one discontinuity is

$$w = \int_0^\infty i_1^2 R dt, \tag{4}$$

where i_1 is the current (a function of time) which would flow in the thermocouple if a single isolated discontinuity occurred in the sample. This current is proportional to the rate of change of induction during this single event,

$$i_1 = A\pi r^2 dB_1/dt, \tag{5}$$

[3] B is used here as an approximation for $B-H$, since in these experiments H is always small compared with B. The apparatus measures changes in $B-H$ rather than in B.

where A is a constant determined by calibrating the apparatus and r is the radius of the sample. Also, for a single impulse the induction will be a function of time,

$$B_1=\frac{8\pi I_s v}{V} f(\tau), \tag{6}$$

where $f(\tau)$ is the same function of time for all impulses (assumption 3) and is determined by the decay of eddy-currents, and v is the volume which changes in magnetization.

Combining Eqs. (4), (5) and (6), and taking the mean value,

$$\overline{w}=64\pi^4 A^2 R I_s^2 r^4 (\overline{v^2}/V^2) \int_0^\infty [f'(\tau)]^2 d\tau .$$

Using also Eqs. (1), (2) and (3), and putting $V/\pi r^2 = l$, the length of the specimen which affects the search coils, we have the result

$$\frac{\overline{v^2}}{\bar{v}}=\frac{l\overline{i^2}}{8\pi^2 A^2 I_s r^2 dB/dt \int_0^\infty [f'(\tau)]^2 d\tau} . \tag{7}$$

The function $f(\tau)$ is subject to the condition that $f(\infty)=1$. Its time deriative, $f'(\tau)$, characterizing the decay of eddy-currents, might be determined experimentally as a function of μ, ρ and r by using a suitable oscillogaph to record the wave-form of the current impulses, caused by single Barkhausen discontinuities, which pass through the thermocouple heater. Since the recording of these wave-forms puts a very severe requirement on the oscillograph, and since it is a laborious undertaking in any case to determine $f'(\tau)$ completely in terms of μ, ρ and r, we have used the expression derived by Wwedensky[4] and supported by experiment. For a spontaneous change in magnetization, we find

$$\int_0^\infty [f'(\tau)]^2 d\tau = \frac{2(10)^9 \rho}{\pi r^2 \mu} , \tag{8}$$

where ρ is the resistivity in ohm-cm, and μ is the permeability which controls the rate of decay of eddy-currents, in this case the reversible permeability or permeability for small alternating fields. Substituting Eq. (8) in Eq. (7),

$$\frac{\overline{v^2}}{\bar{v}}=\frac{l\mu\overline{i^2}}{16\pi(10)^9 A^2 I_s \rho dB/dt} . \tag{9}$$

Wwedensky's expression was derived for a long cylinder the magnetization of which is uniform, consequently Eq. (8) is not strictly applicable to the present problem and must be considered as an approximation. Even if the

[4] B. Wwedensky, Ann. d. Physik **64,** 609–620 (1921).

sudden change in magnetization occurs entirely within a volume small compared to the cube of the radius of the specimen, the disturbance will spread along the axis of the wire to an extent depending on the permeability, resistivity, and diameter of the wire. The extent of the disturbance, necessary for choosing the proper value of l to be used in equation (9), can be determined as described in the next section.

The ratio $\overline{v^2}/\bar{v}^2$ is very near unity for most distribution functions, but may in certain cases be very large. One of us[1] has shown that there are very few discontinuities corresponding to volumes several orders of magnitude smaller than the average. Taking this into consideration, we may with reasonable safety extrapolate to the origin the size distribution curve determined by Tyndall[5] for silicon steel. For the curve so extrapolated we find that $\overline{v^2}/\bar{v}^2=0.7$, a value sufficiently close to unity to make $\overline{v^2}/\bar{v}$, as given by Eq. (9), a reasonably good approximation to $\bar{v}$, the average volume in which we are interested.

All of the quantities on the right-hand side of Eq. (9) can be determined experimentally without unusual difficulties, as described below.

Application to Experiment

Fig. 1 shows the experimental arrangement for measuring $\overline{i^2}$ of Eq. (9). The magnetizing coil, M, is 60 cm long; each search coil is 3.8 cm long, 1.7 cm outside diameter, 0.4 cm inside diameter, and is wound with 10,000 turns of No. 40 B.E.S.S. copper wire. The samples are 60 cm long and 1 mm in diameter. The magnetizing coil is supported on rubber bands in a permalloy shield 5 mm thick to protect it from mechanical and magnetic disturbances. The arrangement for changing the magnetic field slowly and uniformly is that described previously.[1] The amplifier is resistance-capacity coupled with resistances of 70,000 ohms and capacities of one microfarad. For the first stage a screened grid vacuum tube is used (Western Electric 246-A), for the next five stages 239-A tubes, and for the last stage a 104-D tube. The amplification may be varied by using different taps on the input resistance of the second stage. The space current of the last tube passes through the primary of a transformer the secondary of which is connected to the heater of a thermocouple. The impedances of the transformer match respectively the impedances of the vacuum tube in the last stage of the amplifier and the heating element of the thermocouple. The thermocouple is connected to a critically damped Moll galvanometer, G, the deflections of which are recorded on photographic paper mounted on a rotating drum. With this arrangement the deflection δ of the galvanometer, as measured on the paper, is proportional to the mean value of the power expended in the thermocouple heating element, i.e., $\delta \propto \overline{i^2}$.

The mean rate of change of induction, dB/dt, is determined by observing dB/dH and dH/dt separately. To determine dB/dH, the two search coils are connected in series aiding to the Moll galvanometer and the field is changed at a uniform rate. The galvanometer deflection, proportional to

[5] E. P. T. Tyndall, Phys. Rev. **24**, 439–451 (1924).

dB/dH, is recorded photographically as before. The calibration is made by integrating the $dB/dH - vs. - H$ curve and comparing it with the total change in B as determined in the usual way with a ballistic galvanometer. Lines indicating predetermined values of H are marked on the paper by flashing a light when the field-strength passes through these values.

The rate of change of field-strength, dH/dt, is determined by noting with a stop-watch the times at which the needle of the milliammeter in the magnetizing circuit passes through chosen positions.

The reversible permeability μ is determined by subjecting the sample to the small sinusoidal field created in a small single-layer "calibrating coil" inside the search coils and magnetizing coil. A measured current, i_s, of frequency 5 cycles/sec is passed through the calibrating coil, the search coils are connected to the amplifier in series aiding and the deflection of the galvanometer, δ_s, noted for a given value of H, the strength of the steady field produced by the magnetizing coil. The calibration for determining μ is made by removing the sample and observing the deflection δ_c, when a larger current, i_c, of the same frequency passes through the calibrating coil. The permeability may then be calculated as follows. The root mean square current passing through the heater of the thermocouple is proportional to the root mean square rate of change of flux threading the search coils. Since δ is proportional to the square of the current,

$$\delta_s^{1/2} = K i_s(\mu A_s + A_c - A_s),$$

and

$$\delta_c^{1/2} = K i_c A_c,$$

where A_s is the cross-sectional area of the sample, A_c that of the calibrating coil, and K a proportionality constant. The permeability is then given by:

$$\mu = \frac{A_c i_c \delta_s^{1/2}}{A_s i_s \delta_c^{1/2}} - \frac{A_c - A_s}{A_s}$$

and must be determined for various values of H. For the coil and samples used, $A_c = 0.083$ cm^2 and $A_s = 0.0081$ cm^2 so that

$$\mu = \frac{10.2 i_c \delta_s^{1/2}}{i_s \delta_c^{1/2}} - 9.2.$$

The maximum value of the alternating field-strength, calculated from i_s and the number of turns per unit length of the calibrating coil, was kept as low as 0.001 gauss for the more permeable materials.

The values of μ so determined were checked in several cases with those determined with a ballistic galvanometer by measuring ΔB for a change ΔH after several reversals of the field-strength between H and $H + \Delta H$, and extrapolating for the value of $\Delta B/\Delta H$ at $\Delta H = 0$.

The factor A in Eqs. (5) and (9) is the ratio of the current in the thermocouple heater to the rate of change of flux inside the search coils. This is determined by producing a known sinusoidal rate of change of flux in the

calibrating coil and measuring the amplifier output i at the same time. If i_c is the root mean square current in milliamperes through the calibrating coil, f the frequency of the current, n the number of turns of wire per cm, and A_c the cross-sectional area, the root mean square value of the rate of change of flux is

$$(d\phi/dt)_c = 8\pi^2 n A_c f i_c (10)^{-4}$$

and therefore

$$A = \frac{i}{d\phi/dt} = \frac{10^4 i'}{8\pi^2 n A_c f i_c},$$

where i' is the root mean square value of i measured at the same time as i_c. Since i' is proportional to $\delta'^{1/2}$ and i is similarly proportional to $\delta^{1/2}$, we may rewrite Eq. (9) as

$$\frac{\overline{v^2}}{\bar{v}} = \frac{l\mu\delta}{16\pi(10)^9 C^2 I_s \rho dB/dt} \tag{10}$$

where

$$C = \frac{(10)^4 \delta'^{1/2}}{8\pi^2 n A_c f i_c}. \tag{11}$$

The calibrating deflection δ' is recorded on the same paper as the deflections δ caused by the Barkhausen discontinuities. Since the value of C depends on f directly as expressed by Eq. (11) and indirectly through the frequency

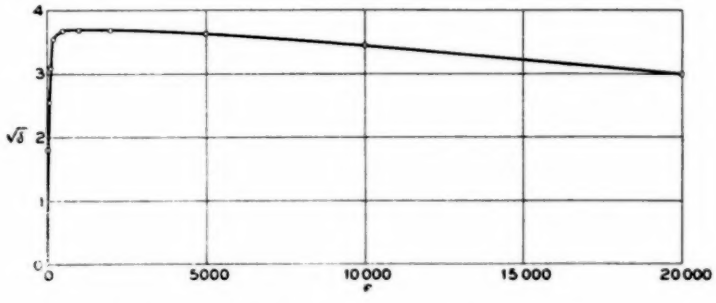

Fig. 2. Frequency characteristics of the apparatus (amplifier, transformer, thermocouple and galvanometer).

characteristics of the apparatus, the amplification was measured for a series of frequencies. At each frequency 0.7 milliampere was passed through a fixed resistance of 0.1 ohm connected to the input of the amplifier in parallel with the search coils, and the deflection of the galvanometer noted. The results are shown in Fig. 2. The range of frequencies shown is sufficient to record accurately the Barkhausen impulses in the materials examined. Calibration was made at the frequency of 60 cycles/sec., and the value of C^2 so obtained has been multiplied by 2 to take account of the lower amplification at this frequency, compared with that in the range of 300 to 5000 cycles.

To determine the length of the sample, l, in which discontinuities will affect the search coils, it is necessary to know how the intensity of a magnetic disturbance decreases with the distance from its source. This was determined experimentally for a disturbance produced by a sinusoidal current flowing in a few turns of fine wire wound directly on a specimen. The law of decay of intensity with distance once determined, it was assumed that the magnetic disturbance caused by a discontinuity in magnetization started at a point and spread along the wire according to this same law. On the basis of this assumption a calculation was made of the change in the observed Barkhausen effect, as measured by the galvanometer deflection δ, when the two search coils (connected in series opposing) were brought closer and closer together,

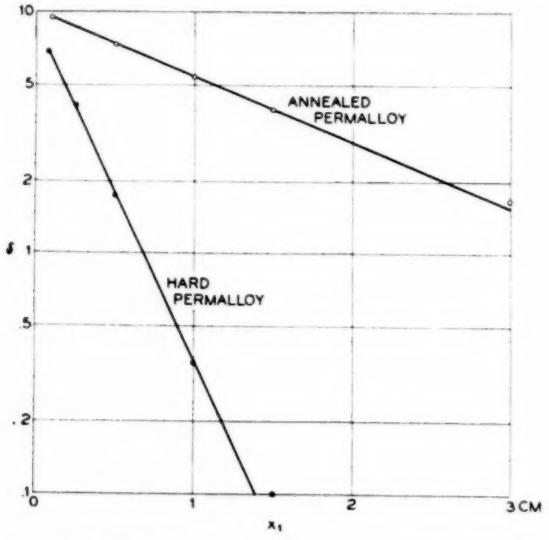

Fig. 3. Decay of magnetic disturbance with distance along wires of different permeabilities.

and this calculation was compared with observation. Ten turns of No. 40 wire were wound closely around the middle of a piece of annealed permalloy containing 81 percent Ni, and a current of 0.5 milliampere of frequency 35 cycles/sec. was passed through it. Two search coils of 0.15 cm inside diameter and 1.3 cm length were placed at equal distances on each side of the 10-turn coil and the deflection δ_1 of the galvanometer noted for various distances x_1 between the small coil and the centers of the search coils. The results (Fig. 3) show that $\delta_1 = C_1 e^{-ax_1}$, where C_1 and a are constants. Assuming that the rate of change of magnetic flux, $d\phi/dt$, at each point along the sample follows this exponential law, and remembering that $d\phi/dt$ is proportional to $\delta^{1/2}$, we have

$$d(\delta)^{1/2} = C_2 e^{-ax/2} dx \tag{12}$$

for each point along the wire. Since the total effect is obtained by adding the value of $\delta^{1/2}$ contributed by each element along the wire, in a search coil of length l_1 we have

$$\delta_1^{1/2} = \int_{x_1 - l_1/2}^{x_1 + l_1/2} C_2 e^{-ax/2} dx \tag{13}$$

or

$$\delta_1 = \frac{4C_2}{a^2}(e^{al/4} - e^{-al/4})^2 e^{-ax_1},$$

agreeing with the experimentally determined relation in that $dln\delta_1/dx_1 = -a$. For the sample described above, $a = 0.60$.

Applying Eq. (12) to the Barkhausen effect, we get Eq. (13) for each discontinuity in magnetization which starts at a point in the sample outside of the search coil. For points inside of the search coil,

$$\delta_1'^{1/2} = \int_0^{x_1 + l_1/2} C_2 e^{-ax/2} dx + \int_0^{x_1 + l_1/2} C_2 e^{-ax/2} dx,$$

and integrating for all points on the sample the galvanometer deflection δ is given by

$$\delta^{1/2} = 2\int_{l_1/2}^{\infty} \delta_1^{1/2} dx_1 + 2\int_0^{l_1/2} \delta_1'^{1/2} dx_1,$$

or,

$$\delta = 16 C_2^2 l_1^2 / a^2. \tag{14}$$

To determine the equivalent length l of Eq. (10), used when two search coils are connected in series opposing, δ is recalculated assuming that all impulses originating at points within a length $l/2$ of the specimen affect all turns of one search coil as much as a real impulse occurring within a search coil affects the turns immediately adjacent. This substitutes for Eq. (12),

$$d(\delta)^{1/2} = C_2 dx, \tag{12'}$$

for Eq. (13)

$$\delta_1^{1/2} = \int_{x_1 - l/2}^{x_1 + l/2} C_2 dx = C_2 l_1, \tag{13'}$$

and for Eq. (14)

$$\delta^{1/2} = \int_0^{l/2} \delta_1^{1/2} dx_1 = C_2 l_1 l/2,$$

or,

$$\delta = C_2^2 l_1^2 l^2 / 4. \tag{14'}$$

Comparison with (14) shows that $l = 8/a$ independent of l_1, the length of each search coil. The value of a is determined experimentally as described above. The data are shown graphically in Fig. 3. A variation in the frequency of the alternating current used in this experiment between 10 and 1000 cycles per

second showed only a slight change in a with frequency. The same experiment was repeated using a hard-drawn wire of the same composition and diameter and a for this sample was found to be 3.22. The ratio of the values of a for these two samples is 5.4, nearly equal to the inverse ratio of the square-roots of their permeabilities, namely $(2510/75)^{1/2}=5.8$. It is concluded that l is proportional to $\mu^{1/2}$, when the resistivity is constant. If the resistivity ρ varies, l must be proportional to $(\mu/\rho)^{1/2}$ since it is only in the ratio μ/ρ that μ and ρ appear in Maxwell's equations. Using the directly determined value of a for the sample with $\mu=2510$ and $\rho=15(10)^{-6}$ ohm-cm, we can therefore finally put

$$l=1.03(10)^{-3}(\mu/\rho)^{1/2}. \tag{15}$$

A more extensive analysis of the dependence of δ on the distance, y, between the two search coils used in measuring the Barkhausen effect, shows that a may also be determined from the relation between δ and y. Such a determination has been made for one sample and found to agree with the determination as described above.

Combining Eq. (14) with Eq. (10) and designating the ratio $\overline{v^2}/\bar{v}$ by v, we have

$$v=\frac{2.0(10)^{-14}\mu^{3/2}\delta}{C^2I_s\rho^{3/2}(dB/dH)(dH/dt)} \tag{16}$$

in which all of the quantities are already known or can be determined as described in this section.

The Experimental Results

The following materials were examined in the form of wires 60 cm long and 0.1 cm in diameter:

Armco iron, hard drawn.

Armco iron, vacuum annealed 2 hrs. at 1000°C, cooled 300°/hr.

Large crystals of Fe[6].

Nickel, vacuum annealed 2 hrs. at 1100°C, cooled 300°/hr.

Permalloy, 80.5 percent Ni, vacuum annealed 1 hr. at 1200°C, 2 min. at 830°C, cooled about 1000°/min.

Permalloy, 78.1 percent Ni, vacuum annealed 1 hr. at 1100°C, cooled about 1000°/hr.

Permalloy, 50 percent Ni, vacuum annealed 2 hrs. at 1100°C, cooled 300°/hr.

Figs. 4 to 6 show the photographically registered curves $dB/dH-vs.-H$ for annealed iron, permalloy with 80.5 percent Ni, and permalloy with 50 percent Ni. In taking the photographs, as described in the previous section, the field-strength was varied slowly enough to enable the galvanometer to follow the gross changes in dB/dH, but not slowly enough to record the

[6] We are indebted to Dr. D. Foster of these Laboratories for these crystals. For their preparation and properties, see Phys. Rev. **33**, 1071 (1929).

individual discontinuities. It will be noticed that when the Barkhausen effect is large the curve is relatively irregular. Two photographs of each curve are reproduced to show that some irregularities are due to chance and are different in each run, and that some are permanent characteristics of the material and are reproduced during each magnetic cycle. Irregularities of both kinds are present but difficult to detect when hysteresis

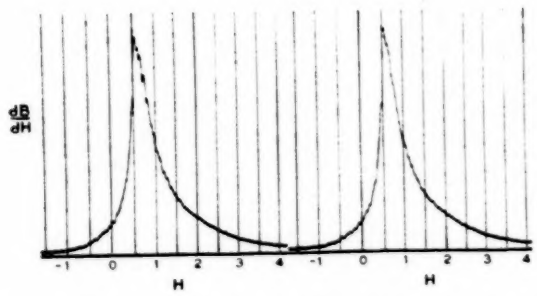

Fig. 4. Galvanometer record of dB/dH for annealed iron.

loops are determined in the usual way with a ballistic galvanometer, small variations from a smooth curve being generally indistinguishable from experimental errors.

The regular procedure was modified slightly for measurements on the large crystals. From a 1 mm wire composed entirely of long crystals, two segments were cut, each 14 cm in length, one containing a single crystal

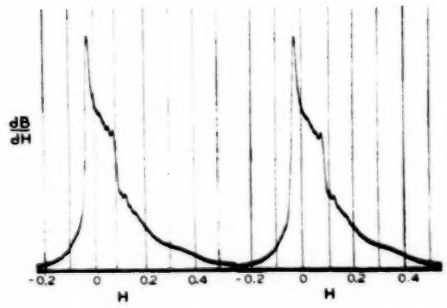

Fig. 5. Galvanometer record of dB/dH for permalloy containing 80.5 percent nickel and 19.5 percent iron.

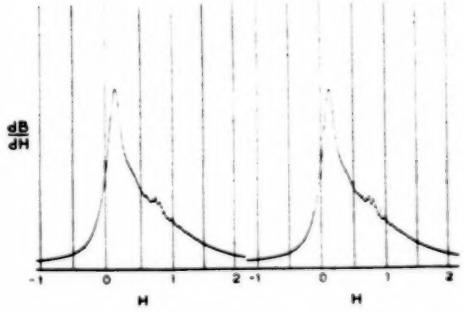

Fig. 6. Galvanometer record of dB/dH for permalloy containing 50 percent nickel and 50 percent iron.

7.2 cm long and the other a single crystal 8.6 cm long, each single crystal occupying the central portion of its segment. The remainder of the two pieces consisted of only four separate crystals, one at each end of the two longest crystals. One search coil was placed around the middle of each of the two segments, the nearest ends of which were 3 cm apart, and measurements of dB/dH, δ, and μ made without moving the specimens of coils.

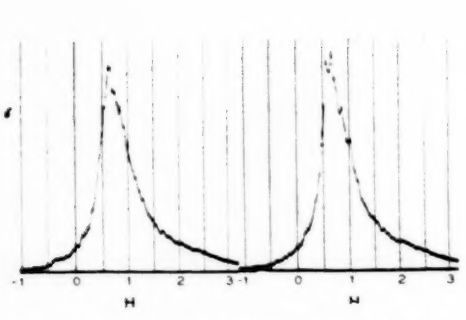

Fig. 7. Record of Barkhausen effect for annealed iron.

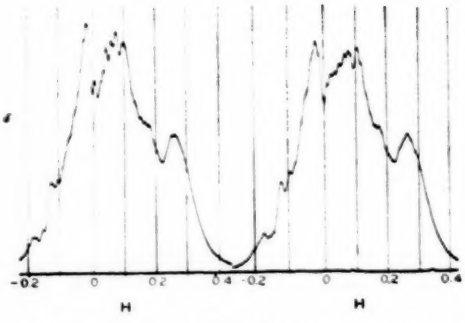

Fig. 8. Record of Barkhausen effect for permalloy containing 80.5 percent nickel and 19.5 percent iron.

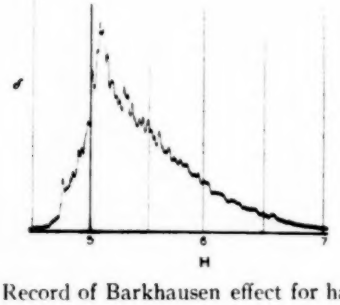

Fig. 9. Record of Barkhausen effect for hard iron.

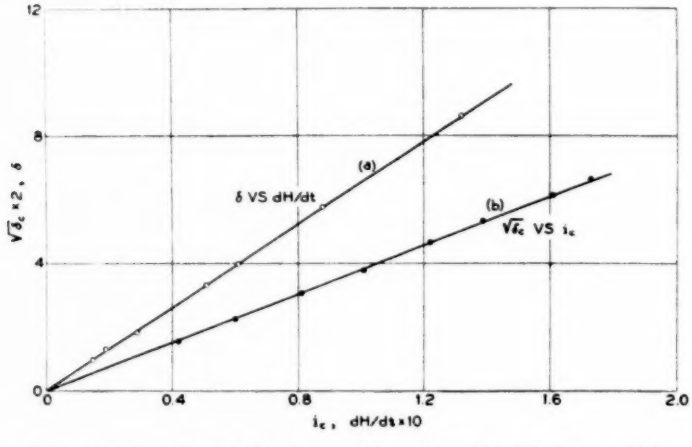

Fig. 10(a) Barkhausen effect in hard permalloy when $H=4.5$, measured by galvanometer deflection δ, as dependent upon rate of change of field-strength. The linear relation shows that the number of the discontinuities depends only on the amount of change of H, and not on dH/dt.

(b) Calibration curve showing that the deflection δ_c is proportional to the square of the calibrating current i_c.

These two crystals are so long that the only discontinuities detected by the coils occurred actually in the crystals.

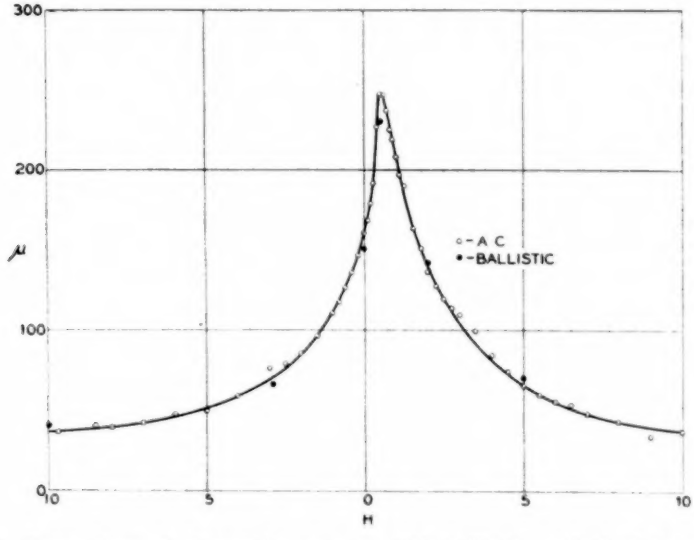

Fig. 11. Comparison of alternating current with ballistic method of determining the permeability for very small alternating fields. The sample is a 1 mm nickel wire, the frequency of the alternating current was 5 cycles/sec., the maximum field-strength during each cycle was 0.006 gauss.

Figs. 7 to 9 are reproductions of the photographically recorded Barkhausen curves, $\delta - vs. - H$, for some of the materials listed above. Duplicate

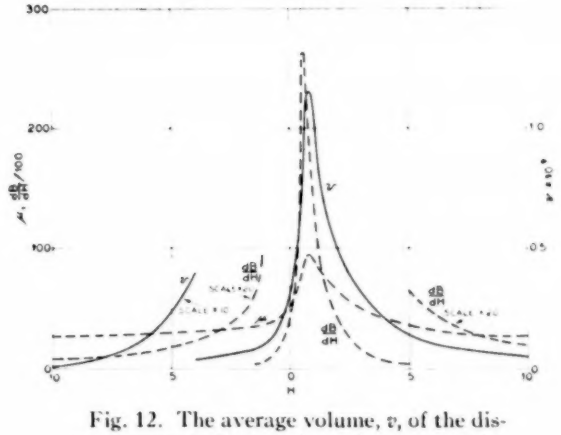

Fig. 12. The average volume, v, of the discontinuities in iron as dependent upon field-strength, and the data used in the determination.

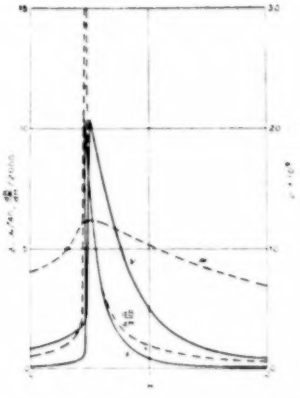

Fig. 13. The v-curve for nickel, and the data from which it was calculated.

runs for annealed iron and permalloy containing 80.5 percent nickel indicate how well the data can be repeated.

According to Eq. (16) the galvanometer deflection δ should be proportional to the rate of change of magnetic field-strength, dH/dt, when the other variables are fixed. Fig. 10(a) shows that this relation was observed, and for

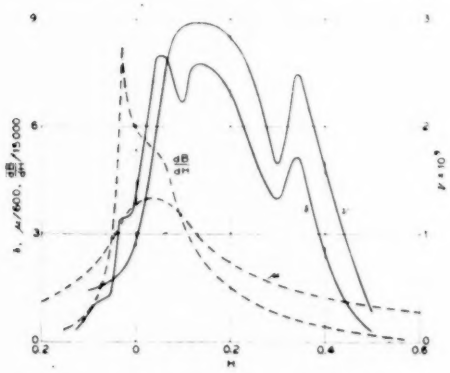

Fig. 14. The v-curve for permalloy containing 80.5 percent nickel and 19.5 percent iron, and the data from which it was calculated.

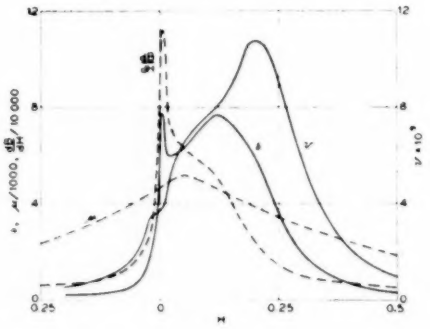

Fig. 15. The v-curve for permalloy containing 78 percent nickel and 22 percent iron, and the data from which it was calculated.

comparison Fig. 10(b) shows the linear relation between the calibrating current, i_c, and the corresponding deflection δ', which appears in Eq. (11).

Fig. 11 shows an example of a $\mu - vs. - H$ curve determined with alternating current of frequency 5 cycles/sec, and for comparison several points determined with a ballistic galvanometer.

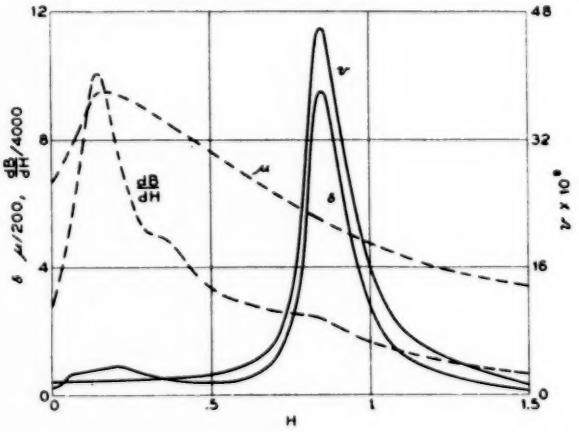

Fig. 16. The v-curve for permalloy containing 50 percent nickel and 50 percent iron, and the data from which it was calculated.

The average volume, v, of the discontinuities in magnetization was calculated in accordance with Eq. (16) for all of the materials. The curves showing v as dependent upon field-strength are shown in Figs. 12 to 18, together with the curves from which the calculations were made. In making

these calculations, small irregularities in the original dB/dH and δ curves were smoothed out, as can be seen for example by comparing Figs. 4, 7, and 12. Finally, Figs. 19 to 25 show how the $v-vs.-H$ curves are placed with respect to the hysteresis loops.

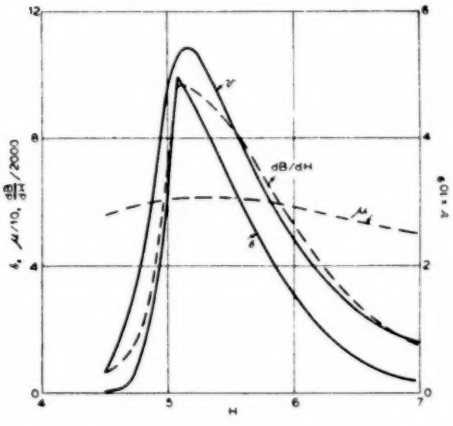

Fig. 17. The v-curve for hard iron, and the data from which it was calculated.

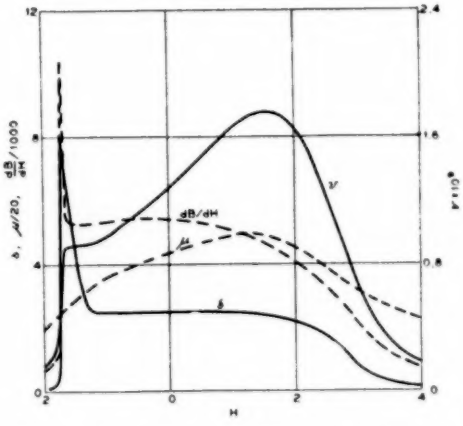

Fig. 18. The v-curve for two single crystals of iron.

Discussion of the Results

Figs. 12 to 18, as well as Figs. 19 to 25, show how the average size of the discontinuities varies from one part of the hysteresis loop to another with

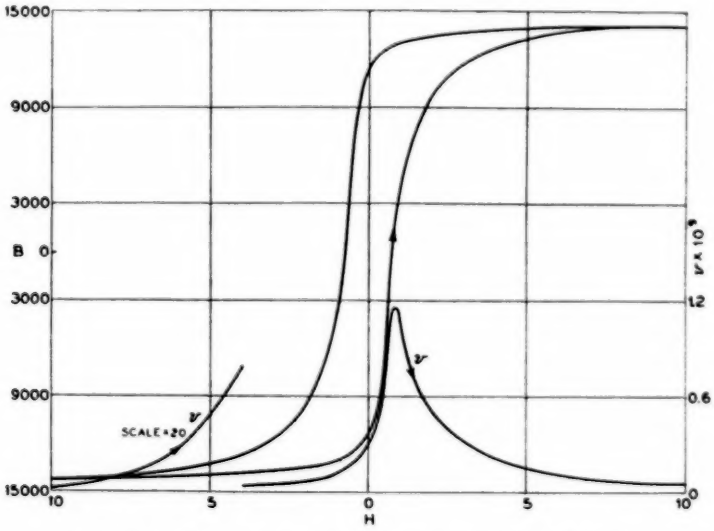

Fig. 19. Hysteresis loop and v-curve for annealed iron.

different materials. The data for annealed iron are more extensive than for the other materials and have been taken over the whole hysteresis loop,

between -10 and $+10$ gauss. When the slope of the hysteresis curve is relatively small, there is some question as to whether the discontinuous changes in magnetization are due to complete magnetic reversals of small

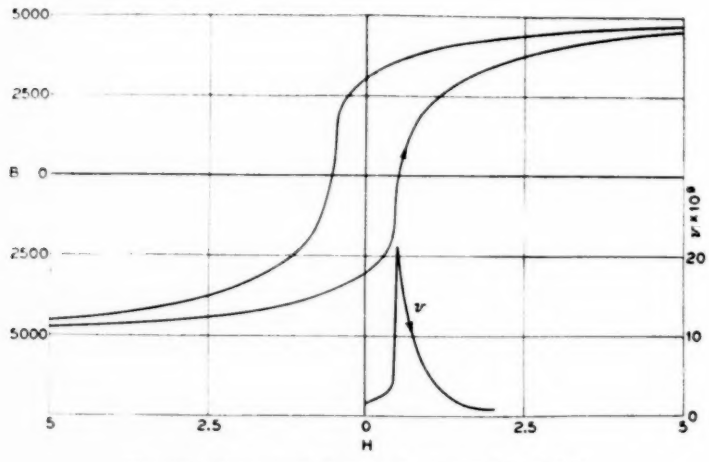

Fig. 20. Hysteresis loop and v-curve for nickel.

parts of the material or whether the reversals are only partially complete, as mentioned in the introduction. Although for this reason the determination of the mean volume of the discontinuities in this case may not be accurate,

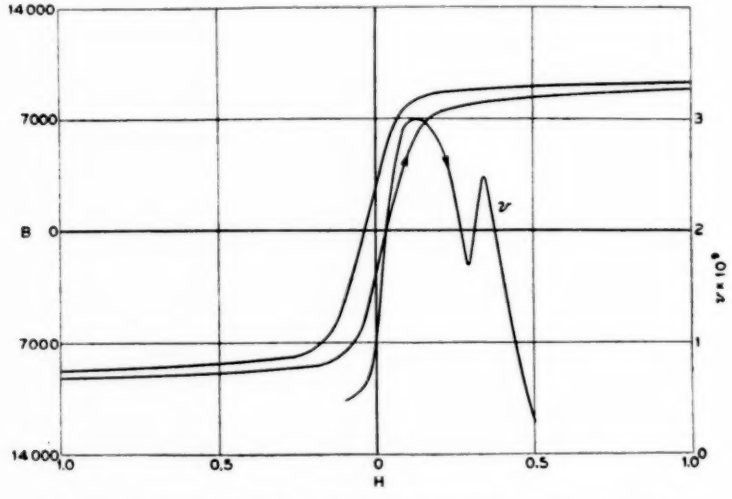

Fig. 21. Hysteresis loop and v-curve for permalloy containing 80.5 percent nickel and 19.5 percent iron.

the data do show, contrary to previous reports, that discontinuities are present throughout the whole cycle. Fig. 26 is a reproduction of the galvanometer record of the Barkhausen effect at the very beginning of the hysteresis

loop for iron, and has been included to show that with sufficiently high amplification the effect is measurable even though dB/dH is as small as 40. It seems possible that the magnetization changes discontinuously in all cases, even

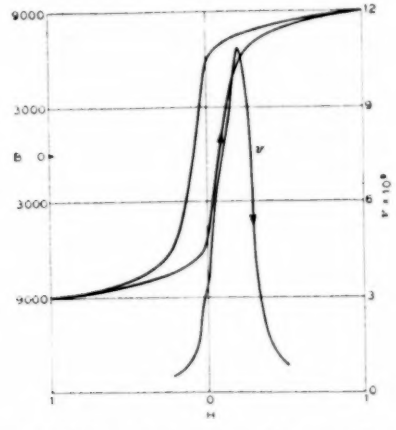

Fig. 22. Hysteresis loop and v-curve for permalloy containing 78 percent nickel and 22 percent iron.

though the material is nearly saturated, and that the discontinuities have been detected only on the steeper parts of the curve because the amplification available has not been sufficient to detect them on the parts less steep.

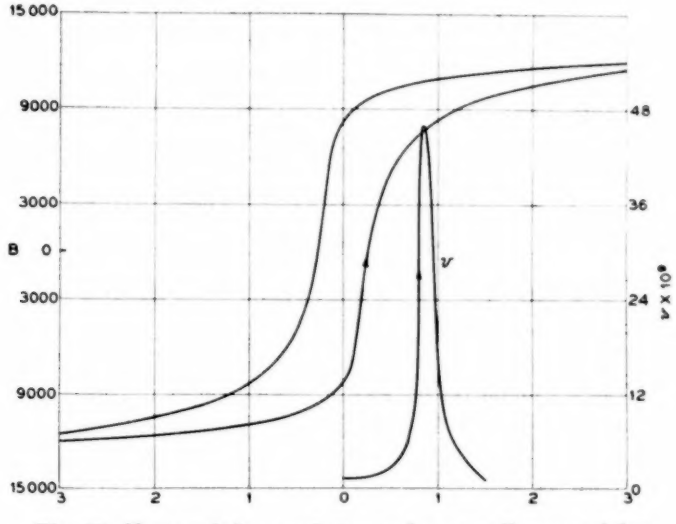

Fig. 23. Hysteresis loop and v-curve for permalloy containing 50 percent nickel and 50 percent iron.

The average volume of material in which the magnetization changes as a unit is found to have a maximum value of the order of $(10)^{-8}$ or $(10)^{-9}$ cm³ for the materials examined. The maximum values vary only from 1.2

$(10)^{-9}$ cm³ for iron to 45 $(10)^{-9}$ cm³ for permalloy containing 50 percent Ni. These volumes are entirely different in order of magnitude from the volume occupied by the crystals in the "single" crystal specimen, which is much

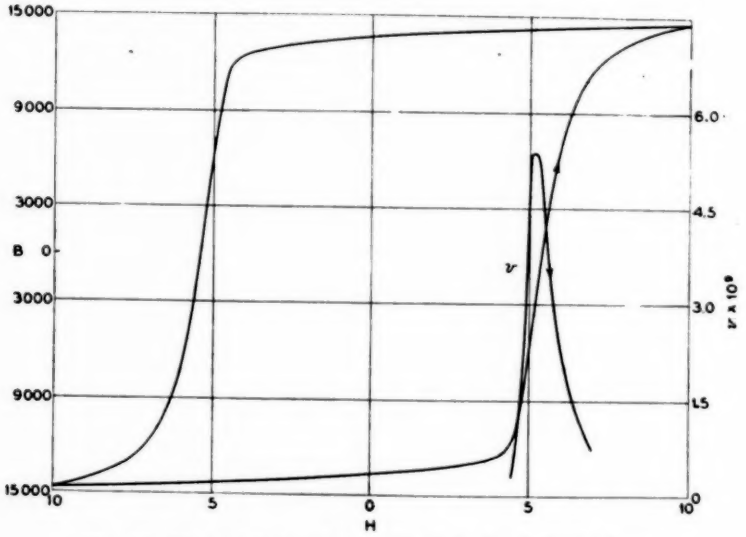

Fig. 24. Hysteresis loop and v-curve for hard drawn iron.

greater; from that occupied by the separate crystals in the hard-worked sample of iron, which is vastly smaller; and also from the volume occupied by a single atom or even by a group of atoms known to be large enough to

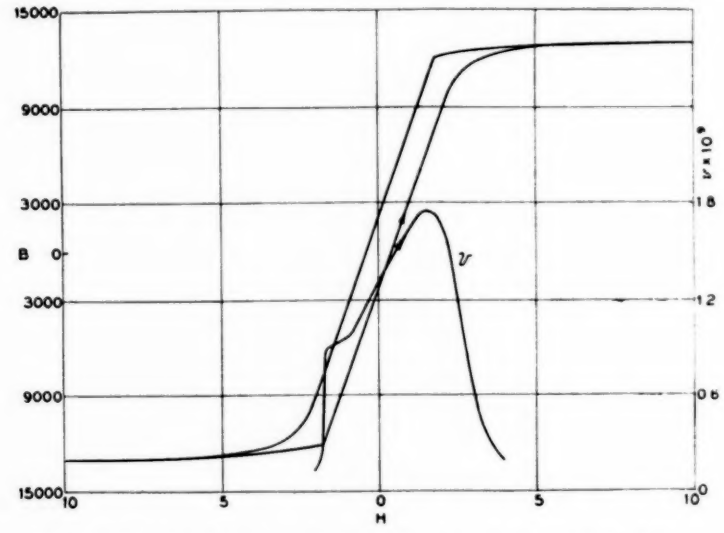

Fig. 25. Hysteresis loop and v-curve for two single crystals of iron.

be oriented by an applied magnetic field, which is very much smaller yet. We regard as a mere coincidence the fact that it is of the same order as the volume occupied by the separate crystals in many well annealed materials.

We conclude that the sizes of the Barkhausen discontinuities are independent of crystal size, and of the nature of the grouping of the atoms of ferromagnetic materials both in respect to the type of lattice upon which the crystal is built, and to the distribution of the different kinds of atoms in alloys.

It is rather surprising at first glance that the computed volumes of the groups should have so nearly the same average value for substances so different. One might expect that, if the magnetization of a group is initiated by the reversal of a single atomic magnet the energy so liberated will aid other magnets to reverse to an extent depending both upon the amount of energy liberated (proportional to the coercive force) and upon the number of other magnets which are about to reverse (proportional to dB/dH). If the coercive force is small and the sides of the hysteresis loop are steep, the initial energy liberated will be small, but there will be a comparatively

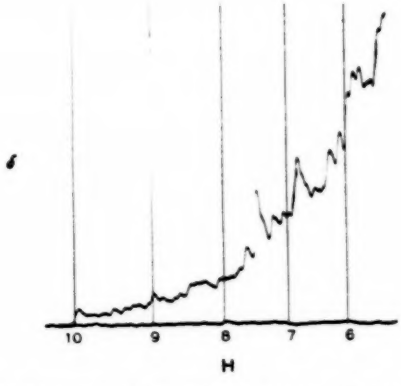

Fig. 26. Barkhausen effect at the beginning of the hysteresis loop for iron, using high amplification

large number of magnets that need but a small disturbance to turn them. If the coercive force is large, the sides of the hysteresis loop are generally less steep. We imagine that these two factors compensate each other, resulting in a relatively constant size of discontinuities in different materials.

The position of the maxima of the $v-vs.-H$ curves for hard and annealed iron and for nickel are near the coercive force, but for the three alloys are definitely displaced to higher values of H. It may be that the positions of these maxima correspond in each case to those for the thermal cooling attending magnetization, observed by Ellwood[7] for steel at magnetizations near the knee of the hysteresis loop.

Our experiments show that the number and size of the discontinuities do not depend on the rate of change of field-strength. As Fig. 10 shows, δ is accurately proportional to dH/dt and this relation implies that the number and size remain constant. For the same total discontinuous change in B, an increase in the average size of the discontinuities and a consequent decrease in their number would be attended by an increase in the ratio of

[7] W. B. Ellwood, Nature **123,** 797–798 (1929).

δ to dH/dt, in contradiction to our findings. Although this linear relation has been found to hold for all of the specimens we have examined, it may not of course hold for the fine wires examined by Heaps and Taylor[8], where the linear extent of the discontinuity is comparable with the diameter of the wire.

Pfaffenberger[9] has reported that the length of the coherence region, within which the discontinuous change is confined, is 3 mm in a steel wire 0.5 mm in diameter. The implication is that during a single discontinuous change in magnetization elementary magnets scattered throughout a volume of about 1 mm^3 are permanently reversed, but that these elementary magnets, if placed next to each other, would occupy a small part, perhaps 10^{-3}, of this volume, corresponding to our volume v. In view of the experiments on the determination of l, described above, we conclude that this 3 mm length is the extent of the region in which the eddy-currents are produced in this sample of steel by the sudden change in magnetization. If Eq. (15) holds for wires 0.5 mm in diameter, we find for Pfaffenberger's sample, using $l/2=0.3$, that $\mu=2.3$. Since Eq. (15) has been established only for wires of radius 0.5 mm, it may be that the more general equation will include some function of the radius. If, for example, the equation is

$$l=1.03(10)^{-3}(\mu/\rho)^{1/2}r^2/(0.05)^2 \qquad (15')$$

we deduce from Pfaffenberger's data that $\mu=10$, a not unreasonable figure for some kinds of steel.

The experiments described above confirm the earlier experiments[1] in showing that for the steeper parts of the hysteresis loop the volume associated with the average discontinuity is very large compared with the dimensions of the atom and seldom involves less than 10^{10} atoms. In annealed materials the average size is comparable with the size of the crystals, but this is regarded merely as a coincidence because the same sized discontinuities are found in hard-worked materials and in a single crystal. The average size is greatest at or near the steepest part of the hysteresis loop and diminishes rapidly as the ends of the loop are approached. The maximum value of the average size (the average size at or near the steepest part of the loop) is about $(10)^{-8}$ cm^3, corresponding to $(10)^{15}$ atoms, and is much the same in the different materials examined.[10]

[8] C. W. Heaps and J. Taylor, Phys. Rev. **34,** 937–944 (1929).

[9] J. Pfaffenberger, Ann. d. Physik **87,** 737–768 (1928).

[10] An interesting paper by F. Preisach, Ann. d. Physik **3,** 737–799 (Dec. 1929) has just come to our attention. His experiments support the previous report by one of us[1] that on the steeper parts of the hysteresis loop almost all of the change in magnetization is discontinuous. Our results disagree in one important respect: Preisach states that when the magnetization diminishes from its greatest value (near to saturation) at one end of the loop, no Barkhausen effect is detectable (with a three stage voice-frequency amplifier) and the change is continuous; we have shown that with sufficiently high amplification (seven stages, wide frequency range) the effect is pronounced, as shown in Fig. 26 above. Preisach has shown that the sizes of the discontinuities in fine wires can be markedly changed by straining them, and that in some cases a single discontinuity corresponds to almost the whole possible change in magnetization of the material. We have also observed such discontinuities in fine unstrained wires of permalloy containing 78 percent nickel and 22 percent iron.

MEASUREMENT OF THE INTENSITY OF HIGH FREQUENCY MAGNETIC FIELDS

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Department of Physics, University of Iowa

(Received January 20, 1930)

Abstract

Two methods are developed for the measurement of the intensity of magnetic fields produced by currents of frequencies from 10 to 25 megacycles.

By the first method, the current in a coil is computed from vacuum tube voltmeter readings of potential drop across a standard inductance. The values for current thus obtained are compared with readings of thermo-ammeters in the range for which they are calibrated. For larger currents, the instruments are shunted and calibrated for particular wave-lengths by the standard inductance method. From these known values of current the intensities of the fields which they produce are computed.

By the second method, the e.m.f. induced in a single turn coil placed in the field to be measured is indicated by a vacuum tube voltmeter. The field intensity necessary to induce the observed e.m.f. is computed. Good agreement is found between the results obtained by the two methods.

Improvements are made in vacuum tube voltmeter design which make possible their use in voltage measurements at frequencies as high as 25 megacycles.

Information regarding current distribution in a coil is obtained.

Introduction

CERTAIN aspects of measuring the intensity of magnetic fields at radio frequency are discussed by a number of investigators. The present work is different from these in that it involves measurements of field intensities in the immediate vicinity of the coil carrying the current and that it includes frequencies as high as 25 megacycles.

Since the audibility of signals in a radio receiving system is a function of the electric and magnetic fields in the vicinity of the receiving antenna, a number of methods of measuring their intensities have been developed. By the use of the siphon recorder, De Groot[1] compared the intensity of static impulses with the intensity of telegraph signals. During the years 1920 and 1921 the Bureau of Standards in an extended series of investigations relative to signal fading used the judgments of 253 observers as to the audibility of the signals in a receiving set as a measure of the intensity of the radiated fields.[2]

Englund and Friis[3] reduced the errors in judging audibility by comparing the intensity of sounds in a receiving set due to the radiated signal with that due to a locally induced e.m.f. of known intensity. Recently, Parlin[4]

[1] De Groot, Inst. R.E. **5,** 93 (1917).
[2] Sci, Pap. B. of S., No. 474 (1923).
[3] Englund and Friis, Trans. Am. Inst. E.E. **46,** 492 (1927).
[4] Parlin, Phys. Rev. **33,** 432 (1929).

has published the results of measurements of the relative intensity and state of polarization of radiated fields at distances of 40 to 100 meters from the oscillator. One important difference between this work and that of earlier investigators is that the intensity is measured by direct galvanometer deflection instead of indirect judgments.

In all the above investigations, the measurements involve the radiated fields some distance from the oscillator rather than in the immediate vicinity of a coil carrying the current.

In dealing with the variation with frequency of the magnetic permeability of certain iron specimens, Wait[5] had occasion to measure the intensity of magnetic fields at the center of a solenoid in the range of wave-lengths from 80 to 1700 meters (more recently[6] in the range from 70 to 120 meters). In this work he used the standard formula $H=4\pi nb/(b^2+a^2)^{1/2}$ for the field intensity at the center of a solenoid of radius a and length $2b$. In the development of this formula it is assumed that the current is uniformly distributed in a cylinder whose length and radius correspond to those of the solenoid and whose thickness is vanishingly small. For the present work this formula does not hold since the dimensions of the coils used depart too far from those assumed.

I. Theory

Computation of field intensity from current. The computation of the intensity of the field about a coil due to a high frequency a.c. in the coil as is done in the case of direct current, is complicated by two factors. First, no instruments are available which will accurately measure high frequency currents of any considerable magnitude; second, the distributed capacity of the coil causes a non-uniformity in the current distribution throughout the coil.

In meeting these difficulties, the measurement of current is accomplished in two ways; first, Weston thermoammeters and thermo-milliammeters with shunts to cover the desired range of current are calibrated at particular frequencies; second, vacuum tube voltmeter readings of the potential drop across standard inductances are taken and from these currents are computed. To eliminate the second complication, a Helmholtz coil of one turn in each section is constructed in which the distributed capacity is sufficiently small that the use of the standard formula[7] for direct current is permissible.

$$H=32\pi ni/5^{3/2}a$$

where n is the number of turns in each section; a is the radius and i is the current in c.g.s. e.m.u.

Computation of field intensity necessary to induce observed e.m.f. in search coil. Since the e.m.f. in a single turn of wire is equal to the rate of change of magnetic flux through the area enclosed by the wire and since the flux is known to vary sinusoidally, the field intensity can be computed if the

[5] Wait, Phys. Rev. **29,** 566 (1927).
[6] Wait, Phys. Rev. **32,** 967 (1928).
[7] S. G. Starling, Elec. & Mag. p. 57.

induced e.m.f. is known. It is obvious then, that vacuum tube voltmeter readings for e.m.f. induced in a single turn coil substituted in the formula developed below yield values for field intensity. The assumption is made that the intensity is uniform throughout the area enclosed by the coil. Such uniformity is available within a Helmholtz coil.

$$e = d\phi/dt$$

where e is the induced e.m.f. and ϕ the flux through enclosed area. Since a sinusoidal field is assumed ϕ may be written $\phi_0 \sin \omega t$ and

$$e_{max} = \phi_0 \omega = 2\pi\nu\phi_0$$

But $\phi_0 = H_0 A$

Then $e_{max} = 2\pi H_{max} \nu A$ (Or r.m.s. value may be used for e and H)

$H = e/2\pi A\nu$ if e.m.u. are used

$H = E \times 10^8/2\pi A\nu$ using volts, gauss and cm^2

Thus we have a formula for H in terms of measurable quantities.

II. Apparatus

Oscillator. The oscillator which proved most satisfactory includes two triodes in push-pull arrangement. The circuit diagram is shown in Fig. 1. The symmetrical feed-in to the main oscillatory circuit C_1L_1 through C_2 and C_3 produced a comparatively pure sine wave current in L_1.

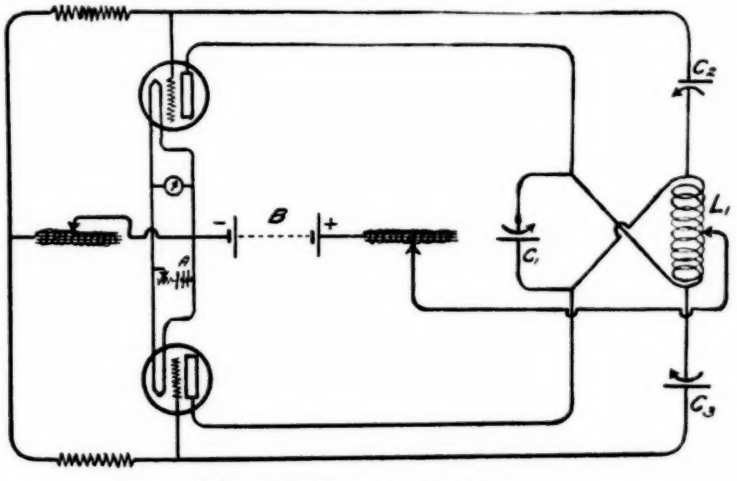

Fig. 1. Oscillator circuit diagram.

The intensity of the output at the first and second harmonics was tested by comparing the readings of the galvanometer of a wave meter tuned to the fundamental with those tuned to the harmonics. The oscillator output was adjusted for full scale deflection of the galvanometer of the wave meter when it was placed several feet from the oscillator. In no case was a deflection of more than a small part of one division (1/100 part of the full scale) noted when the wave meter was tuned to the harmonic frequency and placed one fifth of the above distance from the oscillator.

This circuit is used for three hook-ups. The first, employing seven and one half watt tubes is supplied with seven coils of different numbers of

turns so that a range in wave-length from 5 to 130 meters may be produced. The second, employing fifty watt tubes, covers the range from 5 to 30 meters. The third, employing two hundred fifty watt tubes covers a limited range of 12 to 20 meters.

Pick-up system. The pick-up system in which the current is brought under control is inductively coupled to the oscillator as shown in Fig. 2. L_4 is a one turn coil closely coupled to the output inductance of the oscillator. C_2 and L_5 tune the circuit in which the current is controlled. C_3 and C_1 control the position of the voltage node in circuit C_2L_5. A_1 and A_3 are thermo-ammeter positions. The position A_2 is used variously to meet different demands. In one Helmholtz coil it serves as a thermo-ammeter position. In another Helmholtz coil and in a 5 turn helix it is supplied with gaps for the plug-in standard inductances.

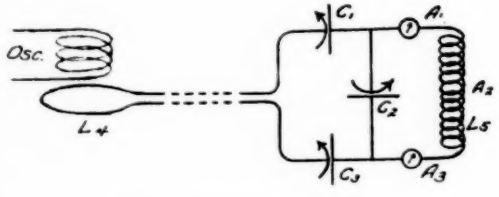

Fig. 2. Pick-up system.

Wave meter. A wave meter including a variable air condenser, an inductance and a Weston thermo-galvanometer to indicate resonance is calibrated by the Lecher wires direct measurement method.[8] It is provided with different size coils to cover the range in wave-length from 5.7 to 32 meters. It is carefully calibrated throughout this range.

Vacuum tube voltmeter. From the large number of vacuum tube voltmeter circuits which are described in the literature[9] the three which gave greatest promise of applicability to measurements at high frequencies were selected for investigation. The first circuit tried out is the vacuum tube multiplier described by M. Y. Colby.[10] The attractive features of this circuit are its flexibility, sensitivity and small power absorption. Several calibration curves run at a frequency of 60 cycles gave satisfactory results in the neighborhood of 100 meters. For wave-lengths much shorter than 100 meters difficulties were encountered and below 20 meters the circuit was found unsatisfactory.

The circuit described by James Taylor[11] gave promise of satisfactory performance. Many calibration curves run at a frequency of 60 cycles were applied in the range of wave-lengths from 30 to 100 meters. Below 30 meters, however the circuit was not satisfacty since the galvanometer and filament leads are directly connected to the high frequency source.

[8] A. Hund, Bureau of Standards, Scientific Paper No. 491.

[9] E. B. Moullin, Radio Frequency Measurements, p. 35. C. R. Cozens, Jour. Sci. Inst. **3**, 181. Van Der Bijl, Thermionic Vacuum Tubes, p. 367. Moullin and Turner, Jour. I.E.E. p. 708, Dec. 1922.

[10] M. Y. Colby, Jour. Sci. Inst. **3**, 342 (1929).

[11] James Taylor, Jour. Sci. Inst. **3**, 113 (1929).

The circuit, Fig 3, which was selected as the most satisfactory for the present work is not found in the literature but has been in use in this laboratory for some time. The deflection of the Leeds and Northrup Galvanometer, G, caused by the d.c. leak off the grid and plate of the vacuum tube is proportional to the charge accumulated thereon. The capacity of C_1 and the resistance of R_1 are not critical but must be sufficiently large as to provide a time constant for the circuit large in comparison with the period of the lowest frequency used. For frequencies greater than 10 megacycles it was found necessary to insert a resistance R_2 to keep the high frequency currents out of the filament battery leads. Since R_2 holds the potential of the galvanometer and filament at the average value of that applied at T_1 (i.e., zero since the applied potential is sinusoidal), the charge on the plate and grid is proportional to the peak value of the potential variation of T_2 rather than the peak value of the potential difference between T_1 and T_2. This requires that T_1 be attached at or near the voltage node of the circuit containing the

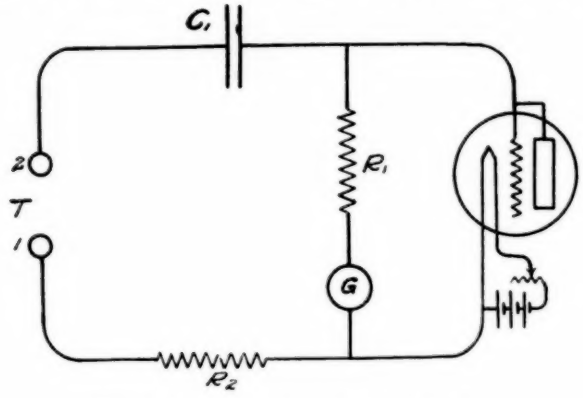

Fig. 3. Vacuum tube voltmeter circuit.

piece of apparatus across which the potential drop is being measured. Fig. 4 shows a typical calibration curve.

From the circuit diagram, Fig. 3, and from the photograph of the instrument, Fig. 5, it is readily seen that an instrument of this type may be designed whose fundamental wave-length is low and which is therefore readily adaptable to high frequency measurements. The total length of wire from T_2 to the grid is 15 cm and the capacity of the vacuum tube is reduced to a minimum by the removal of the base and separation of the leads. To test for the fundamental wave-length of the circuit a thermo-galvanometer was connected across the terminals T, R_2 was shunted by a good conductor and the instrument closely coupled to an oscillator whose output wave-length was varied from 12 to 5.7 meters. No deflection was observed. Similar tests on other instruments whose leads were longer and not so well arranged showed distinct resonance points corresponding to 9 and 16 meters. Thus, it was shown that the natural wave-length of this instrument is somewhat below 5.7 meters.

Helmholtz coils. Two Helmholtz coils were constructed to produce the uniform fields necessary for the search coil method of measurement. The

two differ only in that one is provided with a gap between the turns so that an ammeter may be inserted. The radius of each turn and the distance between the two turns is 8 cm. Substituting these dimensions in the formula (1) for field intensity at the center we get 0.1125 gauss per ampere.

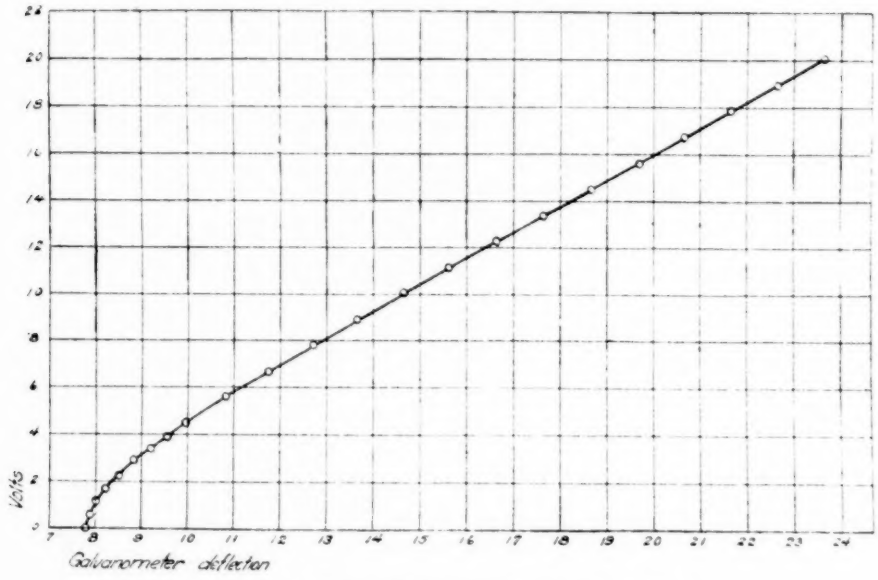

Fig. 4. Vacuum tube voltmeter calibration curve.

Standard inductances. The standard inductances are made from two brass cylinders of different diameters a and b arranged coaxially. One end of each is soldered to the adjacent end of the other by means of a brass disk. To the opposite ends of the two cylinders are attached terminals for plugging

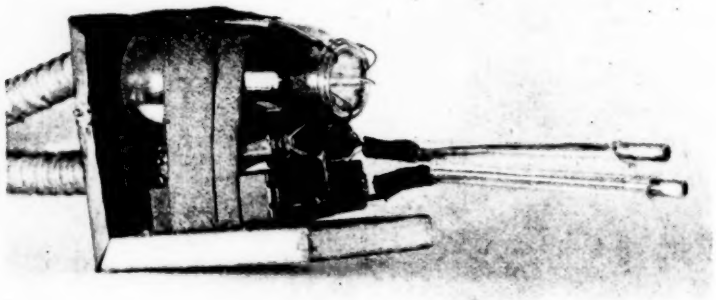

Fig. 5. Vacuum tube voltmeter.

the inductances into the circuit. The numerical value for the inductance was computed from the theory developed in standard texts.[12]

$L = 2 \log_e b/a$ absolute units of inductance per centimeter. Three inductances L_1, L_2, and L_3 were constructed; L is 5 cm long, L_2 is 10 cm, L_3 is 15

[12] Starling, Elec. and Mag. p. 308.

cm. In all three b is 1'' and a is 11/32''. The combination L_3 and L_1 providing a length of 10 cm was most often used.

$L = 10 \times 4.60568 \times 10^3 \log_{10} 1/(11/32) = 0.02137$ henries.

III. Procedure

Measurement of current by potential drop across a standard inductance. The operation of measuring current by the standard inductance method is carried out as follows: Two standard inductances L_1 and L_3 (previously described) are plugged into the center turn of a five turn helix. A vacuum tube voltmeter is connected across L_1. The reading, R_1, of the galvanometer of the vacuum tube voltmeter is taken. L_1 and L_3 are interchanged and the vacuum tube voltmeter reading, R_3, is taken across L_3. $R_3 - R_1$ gives the $I\omega L$ drop across a standard inductance whose length is equal to the difference in length of L_3 and L_1 This subtraction eliminates the end effects, potential variation at T_1 due to improper location of voltage node, pick up by the lead-ins and stray pick up by the vacuum tube voltmeter. From the equation $V = I\omega L$ the corresponding value for current is computed.

Since the standard inductance is essentially a resistance and an inductance in parallel with a capacitance, the potential drop across it is given by the formula:

$$V = I/\{(r^2/\omega^4 L^4) + [(1/\omega L) - \omega C]^2\}^{1/2}$$

For $\lambda = 10$ meters $1/\omega L = 0.247$ and
$\omega C = 0.000981$ which is 0.4% of $1/\omega L$
For $\lambda = 20$ meters $1/\omega L = 0.494$ and
$\omega C = 0.000491$ which is 0.1% of $1/\omega L$

From the equation $r^2 + 4.05^2 = 4.05^2\ (1.01)^2$ we get the value 0.57 ohms which resistance added to WL would increase the impedance by 1 percent. This value is very much greater than the resistance of the standard inductance. We may then drop r and ωC from formula (1) which becomes $V = I\omega L$ as it is used in the preceding paragraph.

Ammeter calibration. Since the use of direct reading instruments is more convenient than the use of the vacuum tube voltmeter with standard inductances, the problem of calibrating thermoammeters was considered. This investigation demanded a solution of the problem of current distribution in the coil since it is not safe to conclude that the current passing through one instrument is the same as that passing through another in a different part of the circuit.

The current distribution throughout the Helmholtz coil was first considered. Three Weston milliammeters, all alike, were placed at the positions A_1, A_2 and A_3 in the pick-up circuit, (see Fig. 2). The oscillator was tuned to different frequencies and the circuit C_2L_5 tuned to resonance with it. Readings were taken at six different wave-lengths from 10 to 30 meters. In all cases when C_1 was larger than C_3, A_1 read smaller than A_3 and the voltage node in the circuit C_2L_5 was nearer C_3 than C_1. Greater differences between C_1 and C_3 always resulted in greater difference between A_1 and A_3 and greater shifting of the voltage node. When C_1 was made smaller than

C_3 the reverse changes were observed. These effects both increased with frequency.

When the five turn helix was substituted for the Helmholtz coil the results were similar but slightly more pronounced. A typical set of data is shown here: C_1, C_2 and C_3 are condenser dial readings in degrees and are essentially proportional to capacities. A_1, A_2 and A_3 are milliampere readings.

TABLE I

C_1	C_2	C_3	A_1	A_2	A_3	Voltage node
41	37	10	84	100.1	115.0	Near A_3
21.4	37	20	103	110.2	115.0	
16.8	37	30	112.6	115.0	115.0	
15.5	37	35	113.1	115.0	113.1	At A_2
14.6	37	40	114.3	115.0	113.1	
13.4	37	50	115.0	114.3	110.2	
12.5	37	60	115.0	113.1	107.0	
12.0	37	70	115.0	112.6	106.0	
11.6	37	80	115.0	112.0	105.0	Near A_1

The above investigation brought out clearly the fact that for instrument calibration the unequal current distribution must be allowed for, the position of the voltage node is a very important factor in current distribution and that the voltage node may be shifted as desired by adjusting C_1 and C_3.

The next step in current measurement was the comparison of current readings by a Weston 115 milliampere thermo-galvanometer with currents computed from vacuum tube voltmeter readings for potential drop across standard inductances.

Thermo-galvanometers were placed at A_1 and A_3, the standard inductances L_1 and L_3 were placed at A_2 with the vacuum tube voltmeter across L_1. When the oscillator had been tuned to the desired wave-length and the pick-up circuit, with the 5 turn helix for L_5, had been tuned to resonance with it, C_1 and C_2 were adjusted so that the voltage node in L_5 was at the filament lead of the vacuum tube voltmeter. This adjustment also made A_1 read the same as A_3. By varying the output of the oscillator, A_1 ($=A_3$) was made to read 115 milliamperes. The reading across L_1 was then taken. L_1 and L_3 were interchanged and the voltage across L_3 was read. Let V_l be the difference between these two readings. Let V_i be the values for voltage across L_3-L_2 computed from the formula $V=I\omega L$ assuming $I=0.115$ amps. From the above operations the following data were obtained:

TABLE II.

λ	V_l	V_i	Diff.
30	0.152	0.155	1.9%
28	0.164	0.166	1.2%
26	0.178	0.179	0.5%
24	0.196	0.194	1.0%
22	0.216	0.212	1.9%
20	0.245	0.233	5.1%
18	0.258	0.258	0.0%
16	0.298	0.291	2.3%
14	0.338	0.333	1.5%

The essential agreement of the above and similar data was interpreted to mean that the thermo-galvanometers are reliable for wave-lengths of fourteen meters and larger.

The precision of Weston thermo-ammeters designed for measurement of larger currents when used for high frequencies may be decreased by either of two factors. First, the capacity between the leads and the instrument case may by-pass a certain amount of current and consequently make the instrument read low. Second, the resistance of the heating element does, no doubt, increase with frequency. Since the deflection is proportional to the power (I^2R) consumed in the heating element any increase in R would make the deflection too large for a given current.

The first effect was easily isolated by comparing readings of a given current with the case on with those after the case had been removed. No effect was observed in the range from 10 to 30 meters except for two instruments designed for mounting with their bases flush with the panel. In these instruments the readings were approximately two percent lower at ten meters with cases on than off. These by-passed currents also expressed themselves in form of heat in the cases when the instruments were shunted and large currents passed through them.

The second effect should be more pronounced in instruments designed for larger currents since their heating elements are made of larger wire. In order to test this factor the 115 milliampere meter was compared with the 250; the 250 with the 500 and the 500 with the one ampere. Then instruments were shunted and calibrated at wave-lengths 12, 20 and 26 meters by comparison with the one ampere instruments. In turn these instruments were compared with a 4 ampere Weston thermo-ammeter. It was found to read slightly high at twenty meters seeming to indicate that the second effect was expressing itself.

The final step in instrument calibration was the comparison of the calibrated instruments against standard inductance values. Table III shows the results.

TABLE III.

λ	I_a	I_L	Diff.
26	1 amp.	0.976	0.024
26	2	2.001	0.001
26	3.5	3.58	0.08

Measurement of field intensity by electromotive force induced in search coil. For this set of measurements the pick-up circuit (Fig. 2) was used with the Helmholtz coil at L_5 and calibrated ammeters at A_1 and A_3. A single turn coil 2.5 centimeters in radius made of fine wire was provided with terminals for plugging it into the vacuum tube voltmeter leads. A short piece of wire just long enough to shunt the leads of the voltmeter thus completing the circle was also provided with plug-in terminals. Reading R_1 was taken with the search coil placed coaxially with the Helmholtz coil and at its center. R_2 was taken with the shunt across the voltmeter leads. The differ-

ence $R_1 - R_2$ gave the e.m.f. induced in a coil of one turn and radius 2.5 centimeters. This value substituted in the formula $H = (E \times 10^8)/\omega A$ gave the values of the field intensity in gauss. Values obtained in this way are listed under H_c in Table IV. Simultaneously with the reading of R_1 and R_2 the current in the Helmholtz coil was read from the calibrated ammeters A_1 and A_2. This reading substituted in the formula $H = 32\pi ni/5^{3/2}a$ also gave values for field intensity at the center of the Helmholtz coil. Values obtained from this substitution are listed under H_a in Table IV.

TABLE IV.

λ	I (amps.)	H_a (gauss)	H_c	Diff.
100	1.0	0.1125	0.1145	1.8%
90	1.0	.1125	.1116	0.8%
80	.96	.1078	.1074	0.4%
70	.93	.1048	.1046	0.2%
60	.88	.0990	.1033	4.1%
50	.79	.0894	.0885	1.0%
40	.66	.0746	.0732	1.8%
30	.115	.0089	.0092	3.3%
20	2.00	.225	.220	2.1%
20	3.00	.337	.330	2.0%
16	2.00	.225	.225	0.0%
16	3.00	.337	.346	2.6%
12	2.00	.225	.217	3.5%

The measurements in the range from 30 to 120 meters were made before the method of controlling the position of the voltage node and the current distribution had been developed. The same refinement and precautions used in the range below 30 meters applied to this range would have given better agreement.

The essential agreement in the values for field intensity obtained by the two methods provides good evidence of the accuracy of both.

IV. Conclusions

1. The vacuum tube voltmeter herein described was applied successfully to the measurement of alternating potentials of frequency as high as 25 megacycles.

2. The standard inductance method provides a satisfactory means of measuring alternating currents of frequencies as high as 22 megacycles.

3. Definite information regarding the distribution of current in a coil was obtained.

4. A comparison of thermo-ammeter readings for high-frequency currents with values obtained by the standard inductance method and with readings of similar instruments made possible their calibration for any desired wave-length above 10 meters.

5. The intensity of a magnetic field within a Helmholtz coil may be computed from known currents in the coil.

6. The intensity of a magnetic field may be computed from the vacuum tube voltmeter measure of e.m.f. induced in a single turn search coil placed in the field.

ON THE FUNDAMENTAL CONSTITUTIVE EQUATIONS IN ELECTROMAGNETIC THEORY

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Abstract

The purpose of this paper is to investigate the absolute significance of the well-known constitutive relations in electromagnetic theory, and to see what simplifications are introduced by various assumptions as to the isotropic character of the space-time continuum. The "linear vector function" expressing the linear relationship between the two fundamental electromagnetic tensors $a_{rs}(\equiv \boldsymbol{B}, c\boldsymbol{E})$ and $b_{ns}(\equiv -\boldsymbol{D}, c\boldsymbol{H})$ is a tensor c_{ns}^{pq} of rank 4 which is covariant and contravariant of rank 2 respectively and is named the "structure-tensor." In order to express mathematically what is meant by the isotropic character of a medium, the notion of orthogonal ennuples is introduced (an orthogonal ennuple defined at a point in space-time enables us to turn the medium in the neighborhood of that point). A tensor is then determined by its invariants with respect to an orthogonal ennuple at the point at which the tensor is taken, rather than by its covariant or contravariant components with respect to the coordinate system of the manifold. The effect of various assumptions as to the isotropic character of space-time on the invariants of the "structure-tensor" c_{ns}^{pq} is investigated and it is found that if space is completely isotropic in the neighborhood of a point P in space-time, then the simple constitutive relations $\boldsymbol{B}=\mu\boldsymbol{H}$ and $\boldsymbol{D}=\epsilon\boldsymbol{E}$ (with μ and ϵ independent of one another) hold; and that to an observer in space-time this fact is indicated by a time-direction 4-vector issuing from P. Since μ and ϵ are distinct only in places where matter is present we can say that the distribution of matter in space-time is affected by the distribution of these time-direction vectors in space-time. The corresponding constitutive relations $\boldsymbol{B}=\mu\boldsymbol{H}$ and $\boldsymbol{D}=\epsilon\boldsymbol{E}$ for empty space (where $\mu\epsilon=1$; Maxwell's relations) are found to hold in the neighborhood of points where these time-direction vectors are absent; i.e. such points are simply geometrical points. The analysis, as introduced in this paper, is a general one and is applied to elasticity theory. Thus the number of distinct coefficients of elasticity appearing in Hooke's law for a transversely-isotropic medium is found to be six instead of five, the reason for this disagreement being that the assumption as to the existence of an energy-density of deformation reduces the number from six to five.

AS IS well known[1] Maxwell's fundamental equations of electromagnetic theory can be very conveniently written in terms of two alternating covariant tensors of rank two (or six-vectors) in space of four dimensions. The first of these, a_{rs} consists of the magnetic induction vector $\boldsymbol{B}$ and the electric intensity vector $\boldsymbol{E}$ in such a way that

$$a_{23}=B_x;\ a_{31}=B_y;\ a_{12}=B_z;\ a_{14}=cE_x;\ a_{24}=cE_y;\ a_{34}=cE_z \qquad (1.0)$$

(c denoting the velocity of light in vacuo) and one set of Maxwell's equations merely expresses the fact that the flux or surface integral of the six-vector

[1] A. Sommerfeld, Ann. d. Physik **32,** 749 (1910); **33** 649 (1910.) H. Bateman, Proc. London Math. Soc. **8,** 223 (1910); F. D. Murnaghan, Phys. Rev **17,** 74 (1921).

a_{rs} across any closed spread of two dimensions, imbedded in the given space-time of four dimensions $(x\ y, z, t)$, is zero. The second fundamental six-vector b_{rs}, consists of the electric displacement (or induction) vector $\boldsymbol{D}$ and the magnetic intensity vector $\boldsymbol{H}$ in such a way that

$$b_{23}=-D_x;\ b_{31}=-D_y;\ b_{12}=-D_z;\ b_{14}=cH_x;\ b_{24}=cH_y;\ b_{34}=cH_z \qquad (1.1)$$

and the second set of Maxwell's equations states that the flux of this six-vector across any closed spread of two dimensions in the given space-time continuum is equal to the volume integral over the space of three dimensions (bounded by the spread of two dimensions) of the current-charge density four-vector. Now, in addition to Maxwell's equations (and quite distinct from them) are certain relations, connecting the four fundamental vectors, $\boldsymbol{B}$, $\boldsymbol{E}$, $\boldsymbol{D}$, $\boldsymbol{H}$ which are known as the constitutive equations. In space free from matter Maxwell made the hypothesis that these constitutive equations were

$$\boldsymbol{B}=\boldsymbol{H};\ \boldsymbol{D}=\boldsymbol{E} \qquad (1.2)$$

whilst in a material medium these equations were replaced by

$$\boldsymbol{B}=\mu\boldsymbol{H};\ \boldsymbol{D}=\epsilon\boldsymbol{E} \qquad (1.3)$$

where if the medium is isotropic μ and ϵ are two constants characteristic of the medium and known respectively, as its permeability and specific inductive capacity. If the medium is not isotropic μ and ϵ are linear vector functions so that the equation $\boldsymbol{B}=\mu\boldsymbol{H}$ for instance, is merely an abbreviation for three equations of the form

$$B_x=\mu_{11}H_x+\mu_{12}H_y+\mu_{13}H_z.$$

It is the purpose of the present paper to investigate the general linear relation connecting the two alternating covariant tensors a_{rs} and b_{rs} and to see what simplifications are introduced by various assumptions as to the isotropic character of the space-time continuum. The "linear vector function" expressing this relationship will be a tensor c_{rs}^{pq} of rank four which is covariant of rank two and contravariant of rank two and which may be assumed without any lack of generality, to be alternating in the contravariant and covariant labels separately. Thus we may write

$$b_{rs}=C_{rs}^{\alpha\beta}a_{\alpha\beta} \qquad (1.4)$$

where the Greek labels α, β are summation labels and it is supposed that the summation runs over the six pairs 23, 31, 12, 14, 24, 34 formed from the four numbers 1, 2, 3, 4, $(x=x^1,\ y=x^2,\ z=x^3,\ t=x^4!)$. The most general situation would involve, then, $6\times6=36$ coefficients c_{rs}^{pq}. The tensor c_{rs}^{pq} which is the analogue of the linear vector function of elementary vector analysis will be called the structure-tensor.

In the section of our paper devoted to the investigation of the effect upon the structure-tensor of various assumptions as to the isotropic charac-

ter of space or space-time, we shall disregard the fact that in the application of our analysis with which we are primarily concerned, i.e., the electromagnetic theory, the tensors a_{rs} and b_{rs} are alternating. The reason for so doing is that a similar analysis is useful in other departments of theoretical physics, e.g. elasticity theory, where the tensors involved are not alternating. In elasticity theory they are symmetric, but it will be convenient not to make any special assumption as to the nature of these tensors until later. The structure-tensor c_{rs}^{pq} will accordingly involve 256 $(=16\times16)$! components and the Greek labels in the fundamental relation

$$b_{rs}=c_{rs}^{\alpha\beta}a_{\alpha\beta}$$

are supposed to run, independently, over the values 1, 2, 3, 4.

Mathematical Description of Isotropy[2]

In order to express most conveniently what is meant by the isotropic character of a medium we shall suppose an orthogonal ennuple[3] (ennuple $=n^{p\text{-}le}$; $n=4$) attached to each point of space-time. Denoting the four vectors of this ennuple by ${}_1\lambda$, ${}_2\lambda$, ${}_3\lambda$, ${}_4\lambda$ any one, ${}_r\lambda$ say, of these will be a contravariant vector whose components are ${}_r\lambda^p (p=1, 2, 3, 4)$ and we shall denote the covariant representation of this vector by ${}^r\lambda_p$. Hence we have the relations defining orthogonality

$${}_r\lambda^\alpha {}^s\lambda_\alpha=\epsilon_r^s \tag{1.5}$$

where the ϵ_r^s are a set of invariants or scalar quantities having the values of the components of the unit tensor δ_s^n; i.e. $\epsilon_r^s=0$ if $s\neq r$ and 1 if $s=r$. By means of the tensors ${}_r\lambda$ and ${}^r\lambda$ any tensor may be described in terms of its invariants relative to the ennuple.[4] For a tensor $A_{s_1\ldots s_k}^{r_1\ldots r_j}$ these are

[2] T. Levi-Civita, "Absolute Calculus" Ch. 10 sec. 2.

[3] By an orthogonal ennuple we mean a pyramid (a generalization of the notion of the trihedron) whose edges are mutually orthogonal. The purpose of fixing a set of four mutually orthogonal directions at every point of our space-time is to provide a mechanism for turning space. Turning the coordinate system simply changes the numbers, for example, which determine a point in space-time.

When we say that any one of the edges of an orthogonal ennuple, the rth say, is presented by a contravariant tensor of rank one ${}_r\lambda^p$ $(p=1, 2, 3, 4)$, we may consider these four components to be the direction cosines of the rth direction with respect to the coordinate system (x) of the space-time continuum. Thus, for example, let us consider a space of three dimensions in which everything is referred to a set of rectangular Cartesian axes and suppose that at any point P a rectangular frame is formed by the tangents (directed in the sense of increasing variables) to the space-polar coordinate curves $r=$ variable, $\theta=$ variable and $\phi=$ variable passing through P. Then the tangent line to the $\theta=$ variable curve, for example, is described in the Cartesian coordinate system of our space by three components:

$${}_\theta\lambda^1=\cos\theta\cdot\cos\phi;\quad {}_\theta\lambda^2=\cos\theta\cdot\sin\phi;\quad {}_\theta\lambda^3=-\sin\theta.$$

[4] For example suppose a space-polar trihedron to be fixed at a point P of space and a vector R determined at this point. Let us suppose that the vector R represents a generalized force. Then this force may be determined by its covariant components $(-\partial\psi/\partial r,\ -\partial\psi/\partial\theta,\ -\partial\psi/\partial\phi)$ or by its projections on the directions belonging to the space-polar trihedron at P,

$$i_{s_1\cdots s_k}^{r_1\cdots r_j} = A_{\sigma_1\cdots\sigma_k}^{\rho_1\cdots\rho_j} {}_{r_1}\lambda_{\rho_1}\cdots {}_{r_j}\lambda_{\rho_j}\,{}_{s_1}\lambda^{\sigma_1}\cdots {}_{s_k}\lambda^{\sigma_k} \tag{1.6}$$

from which it immediately follows that

$$A_{n_1\cdots n_k}^{m_1\cdots m_j} = i_{\beta_1\cdots\beta_k}^{\alpha_1\cdots\alpha_j}\,{}_{\alpha_1}\lambda^{m_1}\cdots {}_{\alpha_j}\lambda^{m_j}\,{}_{\beta_1}\lambda_{n_1}\cdots {}_{\beta_k}\lambda_{n_k} \tag{1.7}$$

(In deriving which, one uses the elementary theorem of algebra that since the two sets ${}_r\lambda^s$ and ${}^p\lambda_q$ are reciprocal; i.e. ${}_r\lambda^{\alpha s}\lambda_\alpha = \epsilon_r^s$, it follows that ${}_\alpha\lambda^{r\alpha}\lambda_s = \delta_s^r$). It follows without difficulty that the tensor relation

$$b_{rs} = c_{rs}^{\alpha\beta} a_{\alpha\beta}$$

is equivalent to a similar relation

$$j_{rs} = K_{rs}^{\alpha\beta} i_{\alpha\beta} \tag{1.8}$$

between the univariants of the tensors involved and it is in terms of the invariants K_{rs}^{pq} of the structure-tensor c_{rs}^{pq} that we shall find it convenient to express the conditions of isotropy.

Suppose now, that at any point of our space-time we have a second ennuple ${}_1\mu$, ${}_2\mu$, ${}_3\mu$, ${}_4\mu$ whose direction-vectors are connected with those of the first set by the relations

$${}_r\mu^p = s_{r\alpha}^{\alpha}\lambda^p \tag{1.9}$$

where the scalar coefficients s_q^p are the elements of an orthogonal matrix. We shall say that the ennuple μ is derived from the ennuple λ by a *rotation* if the determinant of the matrix of the s_q^p is 1 and by a *reflexion* if the determinant of this matrix is -1. In fact the covariant presentations of the two ennuples are connected by the relation

$$i\mu_k = s'^{j\alpha}_{\alpha}\lambda_k \tag{2.0}$$

where s' is the conjugate matrix to $s(s'^p_q = s^q_p)$ so that for the μ-ennuple to be also orthogonal it is necessary and sufficient that the product of the matrix s by its conjugate s' should be the unit matrix and this is the definition of an orthogonal matrix.

The relation between the invariants of any tensor relative to the λ and μ ennuples follows at once. Thus if we distinguish the invariants of a tensor relative to the μ ennuple from those relative to the λ ennuple by a superposed bar, we have, taking a covariant tensor a_{rs} of rank two as an illustration.

$$\bar{i}_{rs} = a_{\alpha\beta}\,{}_r\mu^\alpha\,{}_s\mu^\beta = a_{\alpha\beta}s_r{}^\rho\cdot{}_\rho\lambda^\alpha s_s{}^\sigma\cdot{}_\sigma\lambda^\beta = i_{\rho\sigma}s_r{}^\rho s_s{}^\sigma. \tag{2.1}$$

We are primarily interested in the structure-tensor c_{rs}^{pq} and the relation between its invariants relative to the two ennuples is

$$\bar{K}_{rs}^{pq} = \bar{K}_{\alpha\beta}^{\delta\epsilon}\,{}_\delta s^p\,{}_\epsilon s^q\,{}_r s^\alpha\,{}_s s^\beta \tag{2.2}$$

---

i.e. $(-\partial\psi/\partial r,\ -(1/r)(\partial\psi/\partial\theta),\ -(1/r\sin\theta)\,(\partial\psi/\partial\phi))$. These latter three quantities are invariants with regard to changes in the coordinate system but depend on the particular set of orthogonal directions at P.

The medium will be said to be isotropic (with regard to the structure-tensor c_{rs}^{pq}) relative to the given rotation or reflexion if the invariants $\overline{K}$ of the structure-tensor relative to the new ennuple are the same as its invariants relative to the original ennuple i.e. if

$$\overline{K}_{rs}^{pq} = K_{rs}^{pq}.$$

If the invariants $\overline{K}$ keep their numerical values but change their signs under reflexions the medium will be said to be relatively (as opposed to absolutely) isotropic with respect to the structure-tensor.

Isotropy with Regard to Rotations in the Coordinate Planes

Now a rotation through a right angle in the 2–3 plane is described by the matrix

	${}_1\lambda$	${}_2\lambda$	${}_3\lambda$	${}_4\lambda$
${}_1\mu$	1	0	0	0
${}_2\mu$	0	0	1	0
${}_3\mu$	0	−1	0	0
${}_4\mu$	0	0	0	1

so that $s_2^3 = 1$, $s_1^1 = 1$, $s_3^2 = -1$, $s_4^4 = 1$ all the others being zero. Upon substituting these values in the 256 equations

$$K_{rs}^{pq} = K_{\alpha\beta}^{\delta\epsilon} s_\delta^p s_\epsilon^q s_r^\alpha s_s^\beta \tag{2.3}$$

(which express the assumption that the invariants of the structure tensor are not affected by a rotation through a right angle in the 2–3 plane) we find that many of the invariants of the structure-tensor must be zero; thus if $r=1$, $s=1$, $p=3$, $q=1$, the only term in the quadruple summation which is different from zero is that for which $\alpha=1, \beta=1, \delta=2, \epsilon=1$ whence $K_{11}^{31} = -K_{11}^{21}$; similarly $K_{11}^{21} = K_{11}^{31}$ and combining these results we find that $K_{11}^{31} = K_{11}^{21} = 0$. Proceeding in this manner we find that out of the 256 invariants 128 are zero whilst there are 58 relations amongst the remaining 128 so that there are 70 distinct invariants. These may be succintly displayed in the accompanying table where blanks indicate zero values, and where an abbreviation is introduced for K_{rs}^{pq}. Thus for instance, we write aa for K_{11}^{11}; ig for K_{31}^{24} and so on. The key to this notation is given by

$$\begin{vmatrix} 11 & 12 & 13 & 14 \\ 21 & 22 & 23 & 24 \\ 31 & 32 & 33 & 34 \\ 41 & 42 & 43 & 44 \end{vmatrix} \equiv \begin{vmatrix} a & h & g' & u \\ h' & b & f & v \\ g & f' & c & w \\ u' & v' & w' & d \end{vmatrix}$$

TABLE I.

$j \backslash i$	11	22	33	44	23	32	31	13	12	21	14	41	24	42	34	43
11	aa	ba	ba	da	fa	$-fa$					ua	$u'a$				
22	ab	bb	bc	db	fb	$-fc$					ub	$u'b$				
33	ab	bc	bb	db	fc	$-fb$					ub	$u'b$				
44	ad	bd	bd	dd	fd	$-fd$					ud	$u'd$				
23	af	bf	bf'	df	ff	ff'					uf	$u'f$				
32	$-af$	$-bf'$	$-bf$	$-df$	ff'	ff					$-uf$	$-u'f$				
31							gg	$g'g$	$-g'h'$	$-gh'$			vg	$v'g$	vh'	$v'h'$
13							gg'	$g'g'$	$-g'h$	$-gh$			vg'	$v'g'$	vh	$v'h$
12							gh	$g'h$	$g'g'$	gg'			vh	$v'h$	$-vg'$	$-v'g'$
21							gh'	$g'h'$	$g'g$	gg			vh'	$v'h'$	$-vg$	$-v'g$
14	au	bu	bu	du	fu	$-fu$					uu	uu'				
41	au'	bu'	bu'	du'	fu'	$-fu'$					uu'	uu				
24							gv	$g'v$	$g'w$	gw			vv	$v'v$	$-vw$	$-v'w$
42							gv'	$g'v'$	$g'w'$	gw'			vv'	$v'v'$	$-vw'$	$-v'w'$
34							gw	$g'w$	$-g'v$	$-gv$			vw	$v'w$	vv	$v'v$
43							gw'	$g'w'$	$-g'v'$	$-gv'$			vw'	$v'w'$	vv'	$v'v'$

In the application of this analysis to electromagnetic theory the table will have 6 x 6 instead of 16 x 16 constituents. For isotropy as regards rotation through a right angle in the (2, 3) plane it will read

TABLE IA.

$j \backslash i$	23	31	12	14	24	34
23	ff			uf		
31		gg	$-gh$		vg	$-vh$
12		gh	gg		vh	vg
14	fu			uu		
24		gv	$-gw$		vv	$-vw$
34		gw	gv		vw	vv

so that sixteen of the invariants are zero and only twelve of the remaining 20 are distinct.

When, on the other hand, the structure-tensor is symmetric in both its covariant and contravariant labels (a state of affairs which will arise when both of the tensors between which it sets up a linear relationship are symmetric) the columns and rows must coincide with the corresponding columns and rows for which the order of the labels is altered so that instead of $100 = 10 \times 10$ ($10 = 4 + 6$) distinct constituents there remain only 28, the table reading as follows:

TABLE IB.

$j \backslash i$	11	22	33	44	23	31	12	14	24	34
11	aa	ba	ba	da				ua		
22	ab	bb	bc	db	fb			ub		
33	ab	bc	bb	db	$-fb$			ub		
44	ad	bd	bd	dd				ud		
23		bf	$-bf$		ff					
31						gg	$-gh$		vg	vh
12						gh	gg		vh	$-vg$
14	au	bu	bu	du				uu		
24						gv	gw		vv	$-vw$
34						gw	$-gv$		vw	vv

We shall now find the new relations between the 70 distinct invariants of Table I, introduced by a rotation through any angle θ (other than a right angle) in the 2–3 plane. This rotation is described by the matrix

$j \downarrow$ \ $i \rightarrow$	$_1\lambda$	$_2\lambda$	$_3\lambda$	$_4\lambda$
$_1\mu$	1	0	0	0
$_2\mu$	0	$\cos\theta$	$\sin\theta$	0
$_3\mu$	0	$-\sin\theta$	$\cos\theta$	0
$_4\mu$	0	0	0	1

so that $s_1{}^1 = s_4{}^4 = 1$; $s_2{}^2 = s_3{}^3 = \cos\theta$; $s_2{}^3 = \sin\theta$; $s_3{}^2 = -\sin\theta$.

Upon substituting these values in the equations (2.3) and using the results embodied in Table I, we find the following new relations:

$$(a) \qquad 2(K_{22}^{22} - K_{33}^{22} - K_{23}^{23} - K_{32}^{23}) \sin\theta\cos\theta = (K_{23}^{22} + K_{32}^{22})$$

$$(b) \qquad 2(K_{22}^{22} - K_{33}^{22} - K_{23}^{23} - K_{32}^{23}) \sin\theta\cos\theta = -(K_{23}^{22} + K_{32}^{22})$$

from which we have that $K_{22}^{22} = K_{33}^{22} + K_{23}^{23} + K_{32}^{22}$ and $K_{23}^{22} = -K_{32}^{22}$

$$(c) \qquad (K_{22}^{22} - K_{33}^{22} - K_{23}^{23} - K_{32}^{23})(\sin^2\theta - \cos^2\theta) \sin\theta\cdot\cos\theta = 2K_{23}^{22} \sin^2\theta$$

$$(d) \qquad (K_{22}^{22} - K_{33}^{22} - K_{23}^{23} - K_{32}^{23})(\sin^2\theta - \cos^2\theta) \sin\theta\cdot\cos\theta = 2K_{32}^{22} \sin^2\theta$$

so that $K_{23}^{22} = K_{32}^{22}$ which combined with $K_{23}^{22} = K_{32}^{22}$ gives $K_{23}^{22} = K_{32}^{22} = 0$

$$(e) \qquad 2(K_{22}^{22} - K_{33}^{22} - K_{23}^{23} - K_{32}^{23}) \sin\theta\cdot\cos\theta = (K_{23}^{22} - K_{32}^{22}) + (K_{22}^{23} - K_{33}^{23})$$

or combined with the results of a, b, and c gives us

$$K_{22}^{23} = K_{33}^{23}.$$

Thus the new relations between the invariants K_{rs}^{pq} introduced by this rotation through an angle θ (excluding 90°) are

$$K_{22}^{22} = K_{33}^{22} + K_{23}^{23} + K_{32}^{23}; \quad K_{23}^{22} = 0; \quad K_{32}^{22} = 0; \quad K_{22}^{23} = K_{33}^{23}.$$

If we include these relations in Table I we shall have the conditions on the invariants for isotropy with regard to a rotation through any angle in the 2–3 plane. There are thus $70 - 4 = 66$ distinct invariants.

Table IA remains unchanged, whilst Table IB (since $K_{23}^{22} = 0$ and $K_{22}^{22} = K_{33}^{22} + 2K_{23}^{23}$) contains only $28 - 2 = 26$ distinct invariants, when we include the rotation through an angle θ.[5]

[5] We remark that Table IB (disregarding the coefficients involving the 4th index) applies to the case of a tetragonal crystal with one of the edges an axis of symmetry in the sense that the other two edges of the crystal issuing from P and all rays (in the plane of these two edges) which may be made to coincide with either of these edges by a 90° rotation, are equivalent.

If we wish to find the conditions on the invariants for isotropy with regard to a rotation through any angle θ in some other coordinate plane, let us say the 1–2 plane, we may do so by inspection of Table I. We simply replace 23 by 12 and 32 by 21, whilst 1 is replaced by 3; for 3 stands in the same position with respect to 12, as 1 does to 23. For example, the condition $K^{32}_{11} = -K^{23}_{11}$ of table 1 is replaced by the relation $K^{21}_{33} = -K^{12}_{33}$. Similarly, instead of the relations

$$K^{22}_{22} = K^{22}_{33} + K^{23}_{23} + K^{23}_{32}; \quad K^{23}_{23} = K^{22}_{32} = 0; \quad K^{23}_{22} = K^{23}_{33}$$

we have

$$K^{11}_{11} = K^{11}_{22} + K^{12}_{12} + K^{12}_{21}; \quad K^{11}_{12} = K^{11}_{21} = 0; \quad K^{12}_{11} = K^{12}_{22}$$

In this way we may construct a table of invariants such that there will be structural symmetry with regard to any rotation θ in the 1–2 plane.

ISOTROPY WITH REGARD TO COMBINED ROTATIONS IN PLANES 2–3 AND 1–2.

If in addition to symmetry of structure with regard to a rotation through any angle in the 2–3 plane there is structural symmetry with regard to a similar rotation in the 1–2 plane we find without much fresh calculation the table of invariants for structural symmetry in the 2–3 and 1–2 planes. For example the relation $K^{12}_{11} = 0$ of Table I becomes $K^{23}_{33} = 0$ in the table of invariants for the 1–2 plane, both relations holding for the table of invariants for structural symmetry with regard to combined rotations in the 2–3 and 1–2 planes. Proceeding in this way we find that 192 of the 256 invariants are zero whilst of the remaining 64 only 12 are distinct. The following Table II expresses these facts and the symmetry of it shows that there is structural symmetry with regard to combined rotations through any angle in each of the planes 23, 31 and 12.

TABLE II.

$j \downarrow$ / $i \rightarrow$	11	22	33	44	23	32	31	13	12	21	14	41	24	42	34	43
11	aa	ab	ab	da												
22	ab	aa	ab	da												
33	ab	ab	aa	da												
44	ad	ad	ad	dd												
23					ff	ff'					uf	$u'f$				
32					ff'	ff					$-uf$	$-u'f$				
31							ff	ff'					uf	$u'f$		
13							ff'	ff					$-uf$	$-u'f$		
12									ff	ff'					uf	$u'f$
21									ff'	ff					$-uf$	$-u'f$
14					fu	$-fu$					uu	uu'				
41					fu'	$-fu'$					uu'	uu				
24							fu	$-fu$					uu	uu'		
42							fu'	$-fu'$					uu'	uu		
34									fu	$-fu$					uu	uu'
43									fu'	$-fu'$					uu'	uu

with $K^{11}_{11} = K^{11}_{22} + K^{23}_{23} + K^{23}_{32}$

If we include rotations through any angle θ, i.e. the material now possesses an axis of symmetry such that all rays at right angles to this axis are equivalent, the table corresponding to IB contains a less number of coefficients, there being nine in the first case and only six in the second.

Corresponding to Tables IA we have Table IIA with only four distinct invariants and 24, zero.

TABLE IIA.

j \ i	23	31	12	14	24	34
23	*ff*			*uf*		
31		*ff*			*uf*	
12			*ff*			*uf*
14	*fu*			*uu*		
24		*fu*			*uu*	
34			*fu*			*uu*

Similarly, when the structure-tensor is symmetric in both its covariant and contravariant labels we have a Table IIB corresponding to Tables IB. Thus

TABLE IIB.

j \ i	11	22	33	44	23	31	12	14	24	34
11	*aa*	*ab*	*ab*	*da*						
22	*ab*	*aa*	*ab*	*da*						
33	*ab*	*ab*	*aa*	*da*						
44	*ad*	*ad*	*ad*	*dd*						
23					*ff*					
31						*ff*				
12							*ff*			
14								*uu*		
24									*uu*	
34										*uu*

With $K_{11}^{11}=K_{22}^{11}+2K_{23}^{23}$

there being 78 invariants out of the possible 100 zero, whilst of the remaining 22 only 6 are distinct.

In resumé, the three Tables II, IIA and IIB present the surviving invariants under the assumption that the invariants of the structure-tensor are not affected by a rotation through any angle in the 23, 31 and 12 planes.

We shall now consider the most general orthogonal rotation of the 123-space about the 4th direction. That is, we shall investigate the invariants for structural symmetry about the ${}_4\lambda$-axis.

ISOTROPY WITH REGARD TO A GENERAL ROTATION ABOUT THE λ-AXIS

The general rotation of the 123-space about the 4th direction is given by the matrix

	${}_1\lambda$	${}_2\lambda$	${}_3\lambda$	${}_4\lambda$
${}_1\mu$	$s_1{}^1$	$s_1{}^2$	$s_1{}^3$	0
${}_2\mu$	$s_2{}^1$	$s_2{}^2$	$s_2{}^3$	0
${}_3\mu$	$s_3{}^1$	$s_3{}^2$	$s_3{}^3$	0
${}_4\mu$	0	0	0	1

Upon substituting these values in the fundamental equations

$$K_{rs}^{pq} = K_{\alpha\beta}^{\delta\epsilon} {}_{,p} {}_{,q} S_{\delta}^{\alpha} S_{\epsilon}^{\beta} S_{r} S_{s}$$

(using the conditions expressed in Table II) we find the following new relations

$$K_{23}^{14}=\Delta K_{23}^{14};\ K_{23}^{41}=\Delta K_{23}^{41};\ K_{14}^{23}=\Delta K_{14}^{23}\ K_{41}^{23}=\Delta K_{41}^{23}$$

where Δ is the determinant of the matrix of this rotation, namely

$$\Delta=\begin{vmatrix} s_1^1 & s_1^2 & s_1^3 \\ s_2^1 & s_2^2 & s_2^3 \\ s_3^1 & s_3^2 & s_3^3 \end{vmatrix}$$

and since our matrix is an orthogonal one, we have

$$\Delta^2=1 \text{ or } \Delta=\pm 1.$$

If $\Delta=+1$ then the rotation characterizes a movement of a rigid body about a fixed point. If $\Delta=-1$ the change of directions involves reflexion together with rotation.

Isotropy With Regard to a General Rotation About a Point P

We shall now consider the effect on the invariants K_{rs}^{pq}, if in addition to structural symmetry with respect to a general rotation about the λ-direction there is symmetry of structure with regard to a rotation through any angle in, let us say, the 1–4 plane.

Without fresh calculations but simply by inspection of Table I, we see that corresponding to the following relations therein;—$K_{22}^{22}=K_{33}^{33}$; $K_{11}^{33}=K_{11}^{22}$; $K_{22}^{33}=K_{33}^{22}$ we have (for the 1–4 plane) respectively: $K_{11}^{11}=K_{44}^{44}$; $K_{22}^{44}=K_{22}^{11}$; $K_{11}^{44}=K_{44}^{11}$ which when combined with Table II, yield

(*a*) $$K_{44}^{44}=K_{11}^{11};\ K_{11}^{44}=K_{44}^{11}=K_{22}^{11}.$$

Similarly, the relations $K_{31}^{31}=K_{21}^{21}$ and $K_{13}^{31}=K_{12}^{21}$ for the 2–3 plane become respectively, $K_{42}^{42}=K_{12}^{12}$ and $K_{24}^{42}=K_{21}^{21}$ for the 1–4 plane which when taken together with table 2, yield

(*b*) $$K_{14}^{14}=K_{23}^{23} \text{ and } K_{41}^{14}=K_{32}^{23}.$$

Finally, the relations $K_{31}^{24}=-K_{12}^{43}$, $K_{12}^{42}=-K_{21}^{43}$, $K_{24}^{31}=-K_{34}^{21}$ for the 2–3 plane become respectively $K_{42}^{13}=-K_{12}^{43}$, $K_{24}^{31}=-K_{12}^{34}$, $K_{13}^{42}=-K_{43}^{12}$ for the 1–4 plane which, when combined with Table II, yield

(c) $$K_{23}^{14}=K_{14}^{23};\quad K_{23}^{41}=-K_{14}^{23};\quad K_{41}^{23}=-K_{14}^{23}.$$

If now we impose on the invariants K_{ns}^{pq} the conditions that they be unaffected by a general orthogonal rotation of the ennuple (as a whole) about P, the matrix of this rotation being

	$_1\lambda$	$_2\lambda$	$_3\lambda$	$_4\lambda$
$_1\mu$	s_1'	s_1^2	s_1^3	s_1^4
$_2\mu$	s_2'	s_2^2	s_2^3	s_2^4
$_3\mu$	s_3'	s_3^2	s_3^3	s_3^4
$_4\mu$	s_4'	s_4^2	s_4^3	s_4^4

we find upon substitution in the fundamental equations $K_{ns}^{pq}=K_{\alpha\beta}^{\delta\epsilon}s^{\prime p}{}_{\delta}s^{q}{}_{\epsilon}s^{\alpha}_{r}s^{\beta}_{s}$ taking into account the conditions expressed by Table II and (a), (b) and (c) above, that the new relation obtained is simple

$$K_{14}^{23}=\Delta\cdot K_{14}^{23}$$

where

$$\Delta=\begin{vmatrix} s_1^1 & s_1^2 & s_1^3 & s_1^4 \\ s_2^1 & s_2^2 & s_2^3 & s_2^4 \\ s_3^1 & s_3^2 & s_3^3 & s_3^4 \\ s_4^1 & s_4^2 & s_4^3 & s_4^4 \end{vmatrix}=\pm 1.$$

These results are best expressed in Tables III, IIIA and IIIB corresponding to Tables II, IIA and IIB. Thus

TABLE III.

j \ i	11	22	33	44	23	32	31	13	12	21	14	41	24	42	34	43
11	*aa*	*ab*	*ab*	*ab*												
22	*ab*	*aa*	*ab*	*ab*												
33	*ab*	*ab*	*aa*	*ab*												
44	*ab*	*ab*	*ab*	*aa*												
23					*ff*	*ff'*					*fu*	*−fu*				
32					*ff'*	*ff*					*−fu*	*fu*				
31							*ff*	*ff'*					*fu*	*−fu*		
13							*ff'*	*ff*					*−fu*	*fu*		
12									*ff*	*ff'*					*fu*	*−fu*
21									*ff'*	*ff*					*−fu*	*fu*
14					*fu*	*−fu*					*ff*	*ff'*				
41					*−fu*	*fu*					*ff'*	*ff*				
24							*fu*	*−fu*					*ff*	*ff'*		
42							*−fu*	*fu*					*ff'*	*ff*		
34									*fu*	*−fu*					*ff*	*ff'*
43									*−fu*	*fu*					*ff'*	*ff*

with $K_{11}^{11}=K_{22}^{11}+K_{23}^{23}+K_{32}^{23}$

so that there are only four distinct invariants remaining.

TABLE IIIA.

j \ i	23	31	12	14	24	34
23	*ff*			*fu*		
31		*ff*			*fu*	
12			*ff*			*fu*
14		*fu*		*ff*		
24			*fu*		*ff*	
34				*fu*		*ff*

there being only two distinct invariants K_{23}^{23} and K_{23}^{14} out of 12 different from zero.

TABLE IIIB.

j \ i	11	22	33	44	23	31	12	14	24	34
11	*aa*	*ab*	*ab*	*ab*						
22	*ab*	*aa*	*ab*	*ab*						
33	*ab*	*ab*	*aa*	*ab*						
44	*ab*	*ab*	*ab*	*aa*						
23					*ff*					
31						*ff*				
12							*ff*			
14								*ff*		
24									*ff*	
34										*ff*

with $K_{11}^{11}=K_{22}^{11}+2K_{23}^{23}$

so that as in table IIB, 78 of the invariants are zero, whilst only two of the remaining 22 are distinct.

APPLICATIONS TO ELECTROMAGNETIC THEORY

a. *Absolute isotropy with regard to a general rotation around the* ${}_4\lambda$*-direction.* This means that $\Delta=+1$. Then from Table IIA, we find the relations between the invariants j_{rs} and i_{rs} of the two alternating covariant electromagnetic tensors b_{rs} and a_{rs} respectively:

$$\begin{aligned} &j_{23}=\alpha i_{23}+\beta i_{14};\quad j_{31}=\alpha i_{31}+\beta i_{24};\quad j_{12}=\alpha i_{12}+\beta i_{34}\quad \text{where}\quad \alpha=K_{23}^{23};\ \beta=K_{23}^{14};\\ &j_{14}=\lambda i_{23}+\gamma i_{14};\quad j_{24}=\lambda i_{31}+\gamma i_{21};\quad j_{34}=\lambda i_{12}+\gamma i_{34}\quad \lambda=K_{11}^{23};\ \gamma=K_{14}^{14}. \end{aligned} \tag{2.4}$$

Equations (2.4) are relations between the invariants j_{rs} and i_{rs} of the two electromagnetic tensors b_{rs} and a_{rs} respectively and are valid for any Riemannian space of four dimensions R_4. If, however, we wish to find the corresponding set of relations between the tensor components we must know definitely the ennuple with respect to which the invariants j_{rs} and i_{rs} are taken.

Suppose that the system of coordinates of our R_4 is an orthogonal-curvilinear one for which the fundamental quadratic form is

$$ds^2=H_1{}^2(dx^1)^2+H_2{}^2(dx^2)^2+H_3{}^2(dx^3)^2+H_4{}^2(dx^4)^2,$$

and furthermore that the ennuple at P coincides with this reference frame. Then, the relations between the invariants j_{rs}, i_{rs} and the corresponding tensors b_{rs}, a_{rs} are such that

$$j_{rs}=b_{rs}/H_rH_s; \quad i_{rs}=a_{rs}/H_rH_s$$

so that corresponding to equations (2.4) between the invariants j_{rs} and i_{rs} we have the following set of relations between the tensors b_{rs} and a_{rs}:

$$\begin{aligned}
&\frac{H_1}{H_2H_3}b_{23}=\frac{H_1}{H_2H_3}\alpha a_{23}+\frac{\beta}{H_4}a_{14}; \quad \frac{1}{H_4}b_{14}=\frac{H_1}{H_2H_3}\lambda a_{23}+\frac{\gamma}{H_4}a_{14}\\
&\frac{H_2}{H_3H_1}b_{31}=\frac{H_2}{H_3H_1}\alpha a_{31}+\frac{\beta}{H_4}a_{24}; \quad \frac{1}{H_4}b_{24}=\frac{H_2}{H_3H_1}\lambda a_{31}+\frac{\gamma}{H_4}a_{24}\\
&\frac{H_3}{H_1H_2}b_{12}=\frac{H_3}{H_1H_2}\alpha a_{12}+\frac{\beta}{H_4}a_{34}; \quad \frac{1}{H_4}b_{34}=\frac{H_3}{H_1H_2}\lambda a_{23}+\frac{\gamma}{H_4}a_{34}
\end{aligned} \tag{2.5}$$

We now recall that the tensor a_{rs} consists of the magnetic induction vector $\boldsymbol{B}$ and the electric intensity vector $\boldsymbol{E}$; whilst the other electromagnetic tensor b_{rs} consists of the electric displacement vector $\boldsymbol{D}$ and of the magnetic force vector $\boldsymbol{H}$. Furthermore, let us suppose that $H_1=H_2=H_3=1$ and that $H_4=ic$ i.e. our space-time is a Galilean one. Then equations (2.5) become simply

$$\begin{gathered}
-\boldsymbol{D}=\alpha\boldsymbol{B}-i\beta\boldsymbol{E} \text{ and } \frac{1}{i}\boldsymbol{H}=\lambda\boldsymbol{B}+\frac{\nu}{i}\boldsymbol{E}\\
\text{or } \boldsymbol{D}=i\beta\boldsymbol{E}-\alpha\boldsymbol{B} \text{ and } \boldsymbol{B}=\frac{1}{i\lambda}\boldsymbol{H}-\frac{\nu}{i\lambda}\boldsymbol{E}
\end{gathered} \tag{2.6}$$

and comparing with the relations $\boldsymbol{D}=\epsilon\boldsymbol{E}+\rho\boldsymbol{B}$; $\boldsymbol{B}=\mu\boldsymbol{H}+\delta\boldsymbol{E}$ we have that $\epsilon=i\beta$, $\mu=1/i\lambda$, $\rho=-\alpha$ and $\delta=-\gamma/i\lambda$ or $\epsilon\mu=\beta/\lambda$ and $\rho/\varsigma=\mu\alpha/\gamma$

b. *Absolute isotropy with regard to a generl rotation about P.* By definition $\overline{K}^{pq}_{rs}=K^{pq}_{rs}$ and $\Delta=+1$ so that from Table IIIA we have the following relations between the invariants j_{rs} and i_{rs}

$$\begin{aligned}
&j_{23}=\alpha i_{23}+\beta i_{14}; \ j_{31}=\alpha i_{31}+\beta i_{24}; \ j_{12}=\alpha i_{12}+\beta i_{34}\\
&j_{14}=\beta i_{23}+\alpha i_{14}; \ j_{24}=\beta i_{31}+\alpha i_{24}; \ j_{34}=\beta i_{12}+\alpha i_{34}
\end{aligned} \tag{2.7}$$

where we now have only two distinct invariants $\alpha=K^{23}_{23}$, and $\beta=K^{23}_{14}$. Corresponding to equations (2.6) we have

$$\begin{gathered}
\boldsymbol{D}=i\beta\boldsymbol{E}-\alpha\boldsymbol{B} \text{ and } \boldsymbol{B}=\frac{1}{i\beta}\boldsymbol{H}-\frac{\alpha}{i\beta}\boldsymbol{E}\\
\text{or } \boldsymbol{D}=\epsilon\boldsymbol{E}+\gamma\boldsymbol{B} \text{ and } \boldsymbol{B}=\mu\boldsymbol{H}+\delta\boldsymbol{E}
\end{gathered} \tag{2.8}$$

where $\mu\epsilon=1$ (Maxwell's relation for the aether), and $\rho/\delta=\mu$ or $1/\epsilon$.

c. *Relative isotropy with regard to a general rotation about the* ${}_4\lambda$*-axis. That is,* $\overline{K}^{pq}_{rs}=-K^{pq}_{rs}$ *with* $\Delta=-1$. Then in Table IIA $K^{23}_{23}=K^{14}_{14}=0$ whilst $K^{14}_{23}=-\Delta K^{14}_{23}=K^{14}_{23}$ and $K^{23}_{14}=-\Delta K^{14}_{23}=K^{23}_{14}$ so that the relations between the invariants j_{rs} and i_{rs} are

$$j_{23}=\beta i_{14};\ j_{31}=\beta i_{24};\ j_{12}=\beta i_{34}$$
$$j_{14}=\lambda i_{23};\ j_{24}=\lambda i_{31};\ j_{34}=\lambda i_{12}$$

where β and λ are distinct invariants (2.9) and corresponding to equations 2.6 we have simply

$$\boldsymbol{D}=i\beta\boldsymbol{E} \text{ and } \boldsymbol{B}=\frac{1}{i\lambda}\boldsymbol{H} \tag{3.0}$$

with $i\beta=\epsilon$ and $i\lambda=1/\mu$; or $\epsilon\mu=\beta/\lambda$.

Equations (3.0) are precisely the ones we wished to investigate and we see that the conditions necessary for them to be valid are a relatively-isotropic medium round the time-direction vector orthogonal to the space R_3 (considered as a hypersurface in space-time).

The equations $\boldsymbol{B}=\mu\boldsymbol{H}$, $\boldsymbol{D}=\epsilon\boldsymbol{E}$ (where μ, ϵ are distinct) are valid wherever matter is present. Considered from the point of view that our space R_3 is a hypersurface in space-time R_4, we may say that if matter is present at a point P in our space-time, this fact is made known to an observer (in space-time) by a time-direction ${}_4\lambda$ attached to this point and orthogonal to the hypersurface R_3.

d. *Relative isotropy with regard to a general rotation about a point P.* Table IIIA with $\overline{K}^{pq}_{rs}=-K^{pq}_{rs}$ and $\Delta=-1$ applies to this case. Corresponding to equations (2.9) we have the following set:

$$\begin{aligned} &j_{23}=\beta i_{14};\ j_{31}=\beta i_{24};\ j_{12}=\beta i_{34}\\ &j_{14}=\beta i_{23};\ j_{24}=\beta i_{31};\ j_{34}=\beta i_{12}\end{aligned} \tag{3.1}$$

where $\beta=K^{23}_{14}$, which in the special case of coincidence between the ennuple at P and a Galilean reference frame attached to P, become

$$\boldsymbol{D}=i\beta\boldsymbol{E} \text{ and } \boldsymbol{B}=\frac{1}{i\beta}\boldsymbol{H} \tag{3.2}$$

or

$$\boldsymbol{D}=\epsilon\boldsymbol{E} \text{ and } \boldsymbol{B}=\mu\boldsymbol{H}$$

with $\epsilon\mu=1$ (Maxwell's relation for empty space). We thus see that when the entire space-time is relatively isotropic, i.e. $\boldsymbol{B}=\mu\boldsymbol{H}$ and $\boldsymbol{D}=\epsilon\boldsymbol{E}$ with $\mu\epsilon=1$, then the fact that *no matter* is present in the neighborhood of the point P (x, y, z, t) is made known to an observer (in space-time) by the absence of a time-direction vector at P, orthogonal to the hypersurface R_3.

Applications to Elasticity Theory

Hooke's law on the linear dependence of stress on strain when the latter is small, says that each of the six components of the stress at any point of a body is a linear function of the six components of the strain at that point.

Thus at each point of our medium we are provided with two symmetric tensors, the stress tensor T_{rs} and the strain tensor e_{rs}. The linear relation between them is expressed by the equation

$$T_{rs} = c_{rs}^{\alpha\beta} e_{\alpha\beta} \qquad (r,s=1,2,3) \quad (3.3)$$

where c_{rs}^{pq} may be assumed, without any loss in generality, to be symmetric in the covariant and contravariant indices separately.

Corresponding to the tensor equation (3.2) we have an invariant equation

$$p_{rs} = K_{rs}^{\alpha\beta} q_{\alpha\beta} \qquad (3.4)$$

where p_{rs}, K_{rs}^{pq} q_{rs} are the invariants of T_{rs}, C_{rs}^{pq}, e_{rs} respectively, with respect to an orthogonal ennuple attached to the point P at which these tensors are defined.

Absolute Isotropy Round an Axis

If the medium possesses structural symmetry round an axis we have what is known as *transverse-isotropy*. We find from Table IIB that in this case there are only six distinct invariants. One finds, however, in the literature on the subject that only five independent coefficients are involved in Hooke's law for transverse-isotropy. This disagreement is due to the fact that we have not assumed the existence of an energy-density of deformation, which assumption would lead us to the equation

$$K_{rs}^{pq} = K_{pq}^{rs}$$

and therefore would reduce the number of distinct coefficients of elasticity from six to five. However, we see that as far as Hooke's law is concerned we have six distinct coefficients.

Absolute Isotropy with Regard to the Entire Space

When the medium possesses structural symmetry round all lines, i.e. there is complete or absolute isotropy, then from Table IIIB (which applies in this case) we see that Hooke's law contains only two independent coefficients of elasticity K_{11}^{11} and K_{23}^{23} which in the familiar notation of Lamé are identified with λ and μ.

THE EQUILIBRIUM BETWEEN MATTER AND RADIATION

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Abstract

The equilibrium concentration of electrons and protons is recalculated on the basis of Dirac's new theory of the nature of the proton; it is found to be exceedingly small, of the same order of magnitude as had been found in previous calculations.

THERE have recently been a number of attempts to calculate the equilibrium between matter and radiation in the universe.[1,2,3] There are two difficulties in these calculations; one of these is the generalization of energy and entropy which must be made before the equilibrium state of the entire universe can be treated; this problem has been discussed in particular by Tolman. The other difficulty is the assignment of entropy to a perfect crystal at the absolute zero; it cannot be regarded as entirely certain that this entropy is equal to that of a perfect vacuum, as is assumed. Nevertheless, all calculations agree in yielding for the final equilibrium state one in which the ratio of the energy in the form of matter to that in the form of radiation is exceedingly small; this ratio is dominated by the exponential factor $e^{-mc^2/kT}$ which completely wipes out the effect of all the other factors; the final state of the universe indicated by these calculations is thus one in which there is practically no matter left.

Quite recently Dirac[4] has proposed a theory of the nature of the proton which seems to call for a new calculation of the equilibrium concentration of matter. Briefly stated, Dirac's theory is that the fundamental unit of matter is the electron; in addition to the usual states in which the electron is observed, there are others in which its mass is negative; in these states its total energy is negative, and in fact becomes more negative as its velocity increases. These negative energy electrons are attracted by ordinary electrons, but ordinary electrons are nevertheless repelled by them. All these properties correspond to solutions of the wave equation of the electron which were previously known, but generally considered extraneous. Dirac proposes the hypothesis that space contains great numbers of these negative energy electrons, which obey the Fermi statistics; the states of lowest energy (highest velocity) are therefore full, but a few of the states of low velocity are not

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[1] Stern, Zeits. f. Elektrochem. **31**, 448 (1925); Trans. Far. Soc. **21**, 477 (1925–6).

[2] Tolman, Proc. Nat. Acad. Sci. **12**, 670 (1926); **14**, 353 (1928).

[3] Zwicky, Proc. Nat. Acad. Sci. **14**, 592 (1928).

[4] Dirac, Proc. Roy. Soc. **126A**, 360 (1930).

occupied; these gaps constitute irregularities in the normal arrangement of space, and are observable. It is evident that the gaps will attract ordinary electrons, and be attracted by them; they will also have in effect a positive energy, since they correspond to the absence of a particle of negative energy.

The most natural assumption is that the total number of electrons in the universe is just equal to the number of cells of negative energy; then at the absolute zero every electron would be in the lowest possible state, there would be complete uniformity throughout space, and the universe would be observationally empty. The problem to be solved is simply that of finding the distribution of electrons among the various cells at higher temperatures; we shall confine our solution to a finite region in which there is flat space-time. The problem then differs from the usual applications of the Fermi statistics chiefly in that there are two continuous ranges of energy values. We divide these ranges into intervals in the usual way, and write for the number of cells in the s^{th} interval of the positive energy range

$$Q_s = 4\pi V/h^3(2m)^{3/2}E_s^{1/2}\Delta E \tag{1}$$

and for the number in the t^{th} interval of the negative energy range

$$Q_t = 4\pi V/h^3(2M)^{3/2}E_t^{1/2}\Delta E. \tag{2}$$

We have included in these formulae a factor 2 arising from the spin, which we suppose exists for all energies, and in (2) we use the observed proton mass M; there is some doubt about the correct procedure at this point; $-M$ is what the chemist would call the partial molal (or partial molecular) mass of the electrons of true mass $-m$; it is the right value to use for the change in mass produced in a system by creating the first proton in it; when another proton is created sufficiently close a different value will be needed. The result of our calculations will be that the concentration of matter is exceedingly small, and M therefore is certainly the correct mass for most purposes, though possibly not for ours; it would not make any important change in the results if m did replace M in (2). Also it is unnecessary to use the correct relativistic expressions for (1) and (2), since all cells of large positive kinetic energy are empty, and all those of large negative kinetic energy are full; the number of cells of these kinds will not be correctly given by our result, but this number does not concern us.

The number of distribution of N_s particles among Q_s cells, using the Fermi statistics, is known to be $Q_s!/N_s!(Q_s-N_s)!$ and hence the number of distributions for the entire system, the numbers N_s and N_t being specified, is

$$W = \prod_s \frac{Q_s!}{N_s!(Q_s-N_s)!} \prod_t \frac{Q_t!}{N_t!(Q_t-N_t)!}. \tag{4}$$

This is to be a maximum subject to the conditons of conservation of charge and of energy. Proceeding in the usual way we have

$$\sum_s \{-\log N_s+\log (Q_s-N_s)\}\delta N_s+\sum_t \{-\log N_t+\log (Q_t-N_t)\}\delta N_t=0 \quad (4)$$

$$\sum_s \delta N_s+\sum_t \delta N_t=0 \quad (5)$$

$$\sum_s (E_s+mc^2)\delta N_s-\sum_t (E_t+Mc^2)\delta N_t=0. \quad (6)$$

Using multipliers e^{α} and e^{β} for (5) and (6) we add these three equations and then require each term in the two sums to vanish. Upon rearranging the necessary conditions we have

$$N_s=\frac{Q_s}{e^{\alpha+(E_s+mc^2)\beta}+1} \quad (7)$$

$$N_t=\frac{Q_t}{e^{\alpha-(E_t+Mc^2)\beta}+1}. \quad (8)$$

It is easily shown in the usual manner that $\partial E/\partial S=1/k\beta$ and since thermodynamics requires $\partial E/\partial S=T$,we have as always in this type of calculation

$$\beta=1/kT. \quad (9)$$

For positive values of α the first term in the denominator of (7) will be very large and (7) may be written approximately

$$N_s=Q_s e^{-\alpha-(E_s+mc^2)/kT}. \quad (10)$$

For values of α not too large the first term in the denominator of (8) will be extremely small and we will have

$$N_t=Q_t\{1-e^{\alpha-(E_t+Mc^2)/kT}\}. \quad (11)$$

We now determine α from the state of electrification of the system. The condition for neutrality is

$$\sum_s N_s=\sum_t (Q_t-N_t) \quad (12)$$

which becomes

$$\sum_s Q_s e^{-\alpha-(E_s+mc^2)/kT}=\sum_t Q_t e^{\alpha-(E_t+Mc^2)/kT}. \quad (13)$$

Upon introducing the values of Q_s and Q_t and replacing the sum by an integral we find

$$(2m)^{3/2}e^{-\alpha-mc^2/kT}\int_0^{\infty} e^{-E/kT}E^{1/2}dE=(2M)^{3/2}e^{\alpha-Mc^2/kT}\int_0^{\infty} e^{-E/kT}E^{1/2}dE \quad (14)$$

or

$$e^{\alpha}=(m/M)^{3/4}e^{(M-m)c^2/2kT}. \quad (15)$$

This value of α is evidently such that the approximations (10) and (11) are justified. Upon inserting (15) and (1) into (10) and integrating we obtain for the number of electrons of positive energy

$$N_+ = \frac{4\pi V}{h^3}(4mM)^{3/4} e^{-(m+M)c^2/2kT} \int_0^\infty e^{-E/kT} E^{1/2} dE$$
$$= 2V\left(\frac{2\pi(mM)^{1/2}kT}{h^2}\right)^{3/2} e^{-(m+M)c^2/2kT}. \tag{16}$$

This then is the number of electrons and also the number of protons which the system contains. It is very closely similar to Stern's result for the number of particles of mass m

$$N = V\left(\frac{2\pi mkT}{h^2}\right)^{3/2} e^{-mc^2/kT}. \tag{17}$$

The vanishingly small amount of matter permitted by this equation has already been pointed out, and our result may be regarded as in some measure supporting the view that if any matter is to be preserved in the final equilibrium of the universe it must be rescued by the tendency of matter toward aggregation. But the evidence of astronomy suggests that the stars are constantly gaining matter in the form of dust and meteors, transforming it into radiation and sending it back into space; this may mean, of course, that the universe cannot save its matter by any device and that it is steadily fading away. On the other hand the evidence of the cosmic rays may be supposed to indicate that in the depths of space radiation is converted back into matter; if this process is occurring it can only mean that the foregoing calculation, and all others of a similar nature, are utterly incorrect.

ON THE INTERACTION OF STARK EFFECT AND ELECTRON SPIN IN ALKALI ATOMS[1]

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Abstract

The Stark effect in alkali metal atoms in weak fields is, on the basis of both theory and experiment, a second order effect. It is shown here on the basis of the quantum mechanics that when the second order Stark effect is large enough to be comparable with the multiplet structure, there appears, due to the interaction of the Stark effect and spin, an effect which, in its influence on the multiplet structure, is not unlike the Paschen-Back effect in the magnetic case. It causes a distortion of the multiplet structure and a redistribution of the intensities of the spectral lines.

Introduction

THE Stark effect in complex atoms has not yet been studied extensively in the light of the quantum mechanics, and some time will probably elapse until its more delicate features will be worked out. However, the general aspects of the effect, especially in case of the alkali atoms, have been worked out, and are confirmed by experiment. A review of this subject was recently given by Ladenburg.[2]

Experimental data available at present with respect to the alkali atoms in weak electric fields, i.e., fields which produce shifts of the spectral lines small compared to the fine structure separations, show that the effect is quadratic, i.e., that the separations between the Stark components of the energy levels are proportional to the square of the external field F. The quadratic nature of the effect may be inferred theoretically, in a more or less classical manner, as follows[3]: The valence electron, which does all the radiating, moves in the field due to the nucleus and the inner electrons. This field may be assumed to be central. Since it deviates from a Coulomb field

[1] An abstract of this paper was given in the program of the April, 1929, meeting of the American Physical Society. Phys. Rev. **33,** 1084 (1929).

[2] R. Ladenburg, Phys. Zeits. **30,** 369 (1929).

[3] This familiar argument is repeated here mostly in order to emphasize that it is not entirely general when the effect of electron spin is considered. For example, it has been shown[4,5] that the conclusions of such an argument do not agree with the deductions of the quantum mechanics in case of hydrogenic atoms: an insipient linear effect is to be expected in these atoms due to the degeneracy caused by the effects of the electron spin. Though the difficult task of detecting the linear effect directly by experiment has not been carried out, and therefore these deductions of the quantum mechanics remain untested directly, the theory has answered in agreement with experiment a related question, that of the metastability of the $2s$ level in atomic hydrogen.

[4] R. Schlapp, Proc. Roy. Soc. **119A,** 313 (1928).

[5] V. Rojansky, Phys. Rev. **33,** 1 (1929).

the orbit of the electron precesses. Due to the precession the electrical center of the atom coincides, on the average, with the nucleus. If a weak external field is applied in the direction Z the behavior of the system is not appreciably altered, and the time average of the excursion z of the valence electron in the Z direction remains zero. Now, the first order energy correction due to the field is given by the time average of Fez, and since this vanishes effects only of orders higher than the first are to be expected.

Explicit formulas for the Stark effect in alkali atoms were calculated on the Bohr theory by Becker and by Thomas.[6] With the advent of the quantum mechanics Unsoeld[7] considered the effect in the light of the new theory for fields insufficient to break down the l–quantization, i.e., for fields which we call weak here. Unsoeld's treatment neglects electron spin, and thus his results should apply strictly only in fields (it is difficult to find a satisfactory adjective for the description of such fields) which are weak if gauged by the effect of l on the energy but are very strong if gauged by the multiplet separations.

The purpose of the present paper is to consider the Stark effect in alkali atoms in weak fields in somewhat greater detail by taking into account the electron spin, and, particularly, to show that as the field becomes sufficiently intense, so that its effects within a doublet become comparable to the doublet separation, there should appear an effect not unlike the Paschen-Back effect in the magnetic case, consisting in a distortion of the multiplet structure and in a redistribution of intensities.[8]

The procedure leading to this conclusion is as follows: The appropriate energy matrix is first set up. Then the approximations to the perturbed energy levels are obtained, not by the general matrix perturbation formulas derived for non-degenerate systems but by actually transforming the energy matrix. In doing this it is found that after the energy matrix has been diagonalized in such a way that no first order terms in F appear off the diagonal it acquires elements whose transition frequencies are those between the components of spin doublets. If, as is the case in light atoms, the spin doublets are narrow the transformed matrix is nearly degenerate[9] and use of methods applicable to degenerate systems leads then to the effect referred to above.

We adopt, with a few unimportant but convenient exceptions, the terminology and notation used in reference 5.

Energy Levels

We write the matrix representing the energy of an alkali atom in a weak electrostatic field in the form

[6] R. Becker, Zeits. f. Physik **9,** 332 (1922); W. Thomas, Zeits. f. Physik **34,** 586 (1925).

[7] A. Unsoeld, Ann. d. Physik **82,** 390 (1927).

[8] The theoretical necessity for such an effect in the alkali atoms was recognized by Professor J. H. Van Vleck, who suggested the problem to the writer.

[9] See Van Vleck's paper "*On the σ-Type Doubling and Electron Spin in Diatomic Molecules,*" Phys. Rev. **33,** 467 (1929). In that paper, especially in Section 4, he develops a procedure for handling a system in which a degeneracy appears only in the higher approximations.

$$\boldsymbol{H}=\boldsymbol{H}_0+\boldsymbol{H}_1=\boldsymbol{H}_0+Fez. \tag{1}$$

Here $\boldsymbol{H}_0$ is the (diagonal) energy matrix of the unperturbed atom, whose elements are the experimental energy levels, which we denote by $H_0(n,m,l,j;\ n,m,l,j)$, or, for brevity, by $H_0(l,j)$. The additional term $\boldsymbol{H}_1=\boldsymbol{Fez}$ is the perturbation term due to the external field F, the matrix $\boldsymbol{z}$ representing the z-coordinate of the valence electron. As the elements of $\boldsymbol{z}$ are diagonal in the axial quantum number m, and as transitions involving a change in the principal quantum number n contribute but a negligible part of the total perturbation, we shall be concerned here only with elements of the form $z(n,m,l,j;\ n,m,l',j')$, which we denote, for brevity, by $z(l,j;\ l',j')$. In writing the elements it is also convenient to eliminate the inner quantum number j through its relation to the azimuthal quantum number l, i.e., $j=l\pm\frac{1}{2}$ (reference 5 employs the inverse elimination). The expressions for the elements of $\boldsymbol{z}$ can be taken over from the theory of the Stark effect in hydrogenic atoms in weak fields, so long as the valence electron is assumed to move in a central field.[10] These expressions are given explicitly in reference 5. With the abbreviations

$$\begin{aligned} &K(\alpha)=-3a_1n(\alpha^2-m^2)^{1/2}/8Z\alpha, \quad L(\alpha)=\left[n^2-(\alpha+\tfrac{1}{2})^2\right]^{1/2},\\ &M(\alpha)=-3a_1n\left\{\left[n^2-(\alpha+\tfrac{1}{2})^2\right]m^2\right\}^{1/2}/4Z\alpha(\alpha+1), \end{aligned} \tag{2}$$

they are, since $Z=1$ in arc spectra:

$$\begin{aligned} &z(l,l-\tfrac{1}{2};\ l-1,l-1\tfrac{1}{2})=2K(l-\tfrac{1}{2})L(l-\tfrac{1}{2});\ z(l,l-\tfrac{1}{2};\ l+1,l+\tfrac{1}{2})=2K(l+\tfrac{1}{2})L(l+\tfrac{1}{2});\\ &z(l,l+\tfrac{1}{2};\ l-1,l-\tfrac{1}{2})=2K(l+\tfrac{1}{2})L(l-\tfrac{1}{2});\ z(l,l+\tfrac{1}{2};\ l+1,l+1\tfrac{1}{2})=2K(l+1\tfrac{1}{2})L(l+\tfrac{1}{2});\\ &z(l,l-\tfrac{1}{2};\ l-1,l-\tfrac{1}{2})=M(l-\tfrac{1}{2}); \qquad z(l,l+\tfrac{1}{2};\ l+1,l+\tfrac{1}{2})=M(l+\tfrac{1}{2}). \end{aligned} \tag{3}$$

Multiplication of these elements by Fe gives the corresponding elements of the matrix $\boldsymbol{H}_1$. Thus for the present purpose the elements of the energy matrix $\boldsymbol{H}$ can be regarded as known.

With these elements on hand one might proceed to calculate the perturbed energy levels of the atom by using the formulas[11]

$$W^{(1)}(n;\ n)=H(n;\ n);\ W^{(2)}(n;\ n)=\sum_k{}'\frac{H(n;\ k)H(k;\ n)}{h\nu_0(n;\ k)};\ \text{etc.},\quad (4a,b,\cdots)$$

where n, or k, is the totality of the quantum numbers defining a state, and where $\nu_0(n;k)$ is the transition frequency of the unperturbed system, pre-

[10] With regard to the assumption of a central field for the valence electron see D. R. Hartree, Proc. Camb. Phil. Soc. **24,** 89 (1928), and J. C. Slater, Phys. Rev. **32,** 339 (1928). With regard to the generality of the Kronig's factors see, for example, E. Wigner, Zeits. f. Physik **43,** 644–646, (1927), for the case without spin; as to the effect of including spin see p. 93 of J. v. Neumann and E. Wigner, Zeits. f. Physik **49,** 73, (1928).

[11] M. Born, W. Heisenberg, and P. Jordan, Zeits. f. Physik **35,** 557 (1926). Since the diagonal elements of our $\boldsymbol{H}$ contain no F, and the off-diagonal elements are all of the first order, we write the formulas in a simplified way.

sumably known from experiment. The direct application of these formulas to $\boldsymbol{H}$ would yield expressions, quadratic in F, for the Stark effect in alkali atoms. An examination of the transformations leading to formulas (4) will, however, presently show that in the case of alkali atoms such a procedure is not necessarily legitimate, and that for certain values of F the expressions obtained by applying (4) to $\boldsymbol{H}$ are inaccurate.

Formulas (4) are the results of the process of diagonalization of a matrix, assumed to be non-degenerate, by means of appropriate canonical transformations, a process which we shall now consider more closely. The standard procedure is to use a transformation matrix of the form $\boldsymbol{S}=\boldsymbol{1}+\lambda\boldsymbol{S}'+\lambda^2\boldsymbol{S}''+\cdots=\boldsymbol{1}+\boldsymbol{S}_1+\boldsymbol{S}_2+\cdots$. Let $\boldsymbol{H}'$ represent the new energy matrix resulting from the diagonalization of the original matrix $\boldsymbol{H}$ to terms in F^2. We have:

$$\boldsymbol{H}'=(1+\boldsymbol{S}_1)\boldsymbol{H}(1+\boldsymbol{S}_1)^{-1}=(1+\boldsymbol{S}_1)(\boldsymbol{H}_0+\boldsymbol{H}_1)(1-\boldsymbol{S}_1+\boldsymbol{S}_1{}^2-\cdots, \tag{5}$$

where $S_1(n;m)=H_1(n;m)/h\nu_0(n;m)$. Neglecting terms in F^3, we have

$$H'(n;m)=H_0(n;m)+[H_1(m;m)-H_1(n;n)]\frac{H_1(n;m)}{h\nu_0(n;m)}+\sum_k{}''\frac{H_1(n;k)H_1(k;m)}{h\nu_0(n;k)},$$

where the double dash is used in Σ'' to indicate that only terms for which $k\neq n$ and also $k\neq m$ are included in the summation. Since the diagonal elements of our $\boldsymbol{H}_1$ are zero

$$H'(n;m)=H_0(n;m)+\sum_k{}''\frac{H_1(n;k)H_1(k;m)}{h\nu_0(n;k)}.$$

The elements of $\boldsymbol{H}'$ are found to correspond to transitions:

$(l,l-\frac{1}{2})\rightarrow(l,l-\frac{1}{2})$; $(l-2,l-1\frac{1}{2})$; $(l-2,l-2\frac{1}{2})$; $(l+2,l+1\frac{1}{2})$; and $(l,l+\frac{1}{2})$;

$(l,l+\frac{1}{2})\rightarrow(l,l+\frac{1}{2})$; $(l+2,l+1\frac{1}{2})$; $(l+2,l+2\frac{1}{2})$; $(l-2,l-1\frac{1}{2})$; and $(l,l-\frac{1}{2})$

The elements which will prove of particular interest are:[12]

$$H'(l,l\pm\tfrac{1}{2};l,l\pm\tfrac{1}{2})=\frac{4F^2e^2}{h}\left[\frac{K^2(l\pm\frac{1}{2})L^2(l-\frac{1}{2})}{\nu_0(l,l\pm\frac{1}{2};l-1,l-1\pm\frac{1}{2})}+\frac{K^2(l+1\pm\frac{1}{2})L^2(l+\frac{1}{2})}{\nu_0(l,l\pm\frac{1}{2};l+1,l+1\pm\frac{1}{2})}\right.$$
$$\left.+\frac{M^2(l\pm\frac{1}{2})}{4\nu_0(l,l\pm\frac{1}{2};\ l\pm1,l\pm\frac{1}{2})}\right]+H_0(l,l\pm\tfrac{1}{2})=F^2A_{3/2\pm1/2}+B_{3/2\pm1/2}, \tag{7}$$

and

$$H'(l,l\pm\tfrac{1}{2};l,l\mp\tfrac{1}{2})=\frac{2F^2e^2K(l+\frac{1}{2})}{h}\left[\frac{L(l\mp\frac{1}{2})M(l\mp\frac{1}{2})}{\nu_0(l,l\pm\frac{1}{2};l\mp1,l\mp\frac{1}{2})}\right.$$
$$\left.+\frac{L(l\pm\frac{1}{2})M(l\pm\frac{1}{2})}{\nu_0(l,l\pm\frac{1}{2};\ l\pm1,l\pm\frac{1}{2})}\right]=F^2C_{3/2\pm1/2}. \tag{8}$$

[12] In (7), or in (8), either the upper or the lower of the double signs is to be taken throughout, the subscripts of A, B, and C included.

Application of (4a) to $\boldsymbol{H}'$ yields, of course, the same results as does application of (4a) and (4b) to $\boldsymbol{H}$. To show that the latter procedure is not necessarily accurate it suffices to show that it is not always legitimate to apply (4a) to H'. This, however, follows from the appearance in $\boldsymbol{H}'$ of the "troublesome" elements $H'(l, l\pm\frac{1}{2}; l, l\mp\frac{1}{2})$. Since in the alkali atoms the energy differences between states having different azimuthal quantum numbers are much greater than those between the levels of a spin doublet, the transition frequencies corresponding to these troublesome elements are much smaller than those corresponding to other off-diagonal elements of $\boldsymbol{H}'$. Thus the energy matrix of an alkali atom in a weak electric field, while not strictly degenerate, displays, after being transformed by means of a first order canonical transformation, off-diagonal elements whose perturbing influence cannot be unconditionally disregarded. Formula (4a), on the other hand, disregards entirely the contributions of the off-diagonal elements of a matrix to which it is applied and therefore it cannot be applied directly to $\boldsymbol{H}'$, unless the troublesome elements are themselves negligible due to an extremely small value of the factor F.

To circumvent this difficulty we shift to methods adapted to handling degenerate systems and seek a new transformation matrix $\boldsymbol{T}$, such that in the new energy matrix $\boldsymbol{H}''$, given by

$$\boldsymbol{H}''=\boldsymbol{T}\boldsymbol{H}'\boldsymbol{T}^{-1} \tag{9}$$

all the troublesome elements ($\Delta l=0$, $\Delta j\neq 0$) vanish. Application of (4a) to $\boldsymbol{H}''$ is then legitimate, i.e., the diagonal elements of $\boldsymbol{H}''$ are the required energy levels, correct to terms in F^2.

To determine just the energy levels it is unnecessary actually to evaluate $\boldsymbol{T}$, as the diagonal elements of $\boldsymbol{H}''$ can be found by solving the appropriate secular equation. The procedure is rather simple as in alkali atoms we can neglect the contribution of the elements of $\boldsymbol{H}''$ which are non-diagonal in l, and can thus treat the interaction of the Stark effect and spin within a given spin doublet separately from that in the other spin doublets. We then obtain for each non-vanishing value of l an independent secular equation of the form

$$\begin{vmatrix} H'(l,l-\frac{1}{2};l,l-\frac{1}{2})-W & H'(l,l-\frac{1}{2};l,l+\frac{1}{2}) \\ H'(l,l+\frac{1}{2};l,l-\frac{1}{2}) & H'(l,l+\frac{1}{2};l,l+\frac{1}{2})-W \end{vmatrix}=0. \tag{10}$$

The solutions, in terms of the abbreviated notation of (7) and (8), are, (for $l\neq 0$):

$$W(l,l\mp\tfrac{1}{2})=\tfrac{1}{2}(A_1+A_2)F^2+\tfrac{1}{2}(B_1+B_2) \pm\tfrac{1}{2}\{[(A_1-A_2)F^2+(B_1-B_2)]^2+4C_1C_2F^4\}^{1/2}. \tag{11a}$$

The single energy level ($l=0, j=\frac{1}{2}$) remains unaltered:

$$W(0,\tfrac{1}{2})=H'(0,\tfrac{1}{2};0,\tfrac{1}{2}). \tag{11b}$$

To calculate $W(l, l\mp\frac{1}{2})$ to terms in F^2 we expand the radical in (11a) in powers of F. It is now seen that the consideration of the interaction of the Stark effect and electron spin, embodied in the removal of the "troublesome" elements of $\boldsymbol{H}'$, leads to a distorted multiplet structure. The distortive effect becomes vanishingly small, of course, when $(A_1-A_2)F^2$, (the relative shift of the terms of the spin doublet due to the quadratic Stark effect[13]), is negligible compared to (B_1-B_2), (the spin separation of the doublet in the unperturbed system).

The asymptotic forms of (11a) for small and large values of F are of interest. When F is very small we have, to terms in F^2:

$$W(l,l\mp\tfrac{1}{2})=\tfrac{1}{2}[(1\pm1)B_1+(1\mp1)B_2]+\tfrac{1}{2}[(1\pm1)A_1+(1\mp1)A_2]F^2. \quad (11c)$$

This formula is essentially equivalent to (7). When F is very large the expansion of (11a) becomes, if terms involving reciprocals of F^2 are neglected:

$$W(l,l\mp\tfrac{1}{2})=\tfrac{1}{2}\{A_1+A_2\pm[(A_1-A_2)^2+4C_1C_2]^{1/2}\}F^2$$
$$+\tfrac{1}{2}\{(B_1+B_2)\pm(A_1-A_2)(B_1-B_2)[(A_1-A_2)^2+4C_1C_2]^{-1/2}\}. \quad (11d)$$

If the spin separation is assumed to shrink to zero (11d) goes over into the formula of Unsoeld,[7] as it should.[14]

It was the unsatisfactory aspect of $\boldsymbol{H}'$—its being nearly degenerate—that necessitated the transformation $\boldsymbol{T}$. But is is seen now that this transformation is indispensable whenever the F^2 terms are comparable with the multiplet structure, quite apart from the fact that the spin doublets are narrow. It is not the "absolute" width of the doublet but its "relative" width, as compared to some unit (such as Fea_1) which measures the effect of the field, that is of importance.

Relative Intensities of the Stark Components

For a calculation of the relative intensities of the spectral Stark components it is necessary actually to evaluate the matrix $\boldsymbol{T}$. This is accomplished easiest by again considering singly the matrices of two rows and two columns whose energy determinants are given by (10). The procedure can be simplified still further as follows: The small matrices under consideration are not Hermitian, their two off-diagonal elements being F^2C_1 and F^2C_2. However, the quantity $(C_1-C_2)/(C_1+C_2)$ is very small, of the order of magnitude of the ratio $\nu_0(\Delta l=0,\ \Delta j\neq0)/\nu_0(\Delta l\neq0)$. We can thus introduce a new quantity C, defined by $C^2=C_1C_2$, and *set* $C_1=C_2=C$, without reducing the order of accuracy employed in the calculations above. (These approximations are not intrinsically necessary, and are employed only to attain simplicity in the final formulas for the elements of $\boldsymbol{T}$). When these approximations are made in $\boldsymbol{H}'$ the small matrices become Hermitian, but their eigenvalues are not al-

[13] In view of (11a) this is only approximately so.

[14] It must be noted that the quantum number which Unsoeld denotes by m is denoted by m_l in the notation of reference 5, adopted here. The quantum numbers denoted by m and by m_l, respectively, in the latter notation are related thus: $m=m_l\pm\frac{1}{2}$.

tered. The indeterminateness in $\boldsymbol{T}$ can now be removed by setting $\boldsymbol{T}\tilde{\boldsymbol{T}}^* = \mathbf{1}$, and the non-vanishing elements of $\boldsymbol{T}$, written in terms of (7), (11a), and the quantity C, become:

$$\text{for } l=0: \qquad T(0,\tfrac{1}{2};0,\tfrac{1}{2}) = 1 \tag{12a}$$

$$\text{for } l\neq 0: \qquad T(l,l-\tfrac{1}{2};l,l-\tfrac{1}{2}) = T(l,l+\tfrac{1}{2};l,l+\tfrac{1}{2}) = F^2C/\xi, \tag{12b}$$

$$T(l,l+\tfrac{1}{2};l,l-\tfrac{1}{2}) = -T(l,l-\tfrac{1}{2};l,l+\tfrac{1}{2}) = [H_1-W](l,l-\tfrac{1}{2};l,l-\tfrac{1}{2})/\xi,$$

where

$$\xi = \left[F^4C^2 + \tfrac{1}{4}\left\{[H_1-W](l,l-\tfrac{1}{2};l,l-\tfrac{1}{2})\right\}^2\right]^{1/2}.$$

To calculate the relative intensities of the components we may now proceed as outlined in the first paragraph of Section 11 of reference 5, except that instead of the transformation $\boldsymbol{S}$ given there we must use the successive transformations $\boldsymbol{S}$ and $\boldsymbol{T}$ given in the present paper, formulas (5) and (12).

The interaction effect described above is probably not beyond observation in light atoms.

It is a pleasure for the writer to express here his thanks to Professor J. H. Van Vleck for the suggestion of this problem and for the criticism of this work.

ALTERNATING INTENSITIES AND ISOTOPE EFFECT IN THE BLUE-GREEN ABSORPTION BANDS OF Li_2

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Abstract

Term analysis. The analysis of the blue-green Li_2 bands previously given by Wurm is extended by new data obtained with second order plates from the 15-ft. concave grating. The band heads are given by $\nu_k = 20{,}398.40 + 267.3v' - 3.1v'^2 - 347.4v'' + 2.5v''^2$. Wave-numbers of the rotational structure lines of the (0, 1) band are tabulated, and the evaluation of the rotational term-differences in the lower state completely confirms the assignment of this system to the electronic transition $^1\Pi \leftarrow {}^1\Sigma$. The molecular constants, as completely re-determined from our data, using a more accurate procedure than that of Wurm, agree closely with his values. The new constants resulting from our work are $F_e' = 1.337 \times 10^{-10}$ cm^{-1}, $F_e'' = 1.535 \times 10^{-10}$, $\alpha'' = 0.00744$, and $\beta'' = 0.765 \times 10^{-5}$. By means of the final constants and the theoretical equations, an accurate representation of the wave-numbers of the lines of the (0, 0) band is obtained. The origin of this band is found to be 20,395.96 cm^{-1}.

Isotope effect. The vibrational isotope effect is established by the identification of three band heads (1, 0), (2, 0), and (3, 0), due to the less abundant isotopic molecule, Li^6Li^7, which were found in their calculated positions within the error of measurement. The rotational isotope effect in the (0, 0) band is shown by the detection of two faint line series fitting closely the theoretical equations for the Q and P branches due to Li^6Li^7.

Alternating intensities The alternation ratio of the intensities of successive lines in the Li_2^7 bands is determined by a new method, depending partly on the theory of intensity distribution in this type of bands given by Mulliken. The best value is found from the Q branches of the (0, 0) and (1, 0) band to be 1.78 ± 0.2. A less reliable determination from the (0, 1) band gives 1.50. Evidence is given pointing to the true value as 1.67, which corresponds to a nuclear spin of the Li atom of $3/2(h/2\pi)$. This disagrees with the value $\frac{1}{2}(h/2\pi)$ found from hyperfine structure investigations by Schüler and Brück. As required theoretically, the isotope lines due to the unsymmetrical molecule Li^6Li^7 show no alternation.

CERTAIN interesting features of the absorption bands of lithium vapor have recently been discussed by the writers in two preliminary communications.[1,2] Spectrograms taken with both low and high dispersion showed that with a suitable adjustment of the density of the absorbing vapor, the vibrational and rotational structures of the blue-green system are simple enough to permit the quantum analysis. The close analogy of these bands with the corresponding Na_2 system[3] led us to ascribe them to a transition from a $^1\Sigma$ normal state to a $^1\Pi$ excited state. This is in harmony with the observed simple PQR

* Commonwealth Fund Fellow.

[1] A. Harvey and F. A. Jenkins, Phys. Rev. **34,** 1286 (1929) (Quantum structure, alternating intensities).

[2] A. Harvey and F. A. Jenkins, Phys. Rev. **35,** 132 (1930), Abstract, (Vibrational isotope effect).

[3] F. W. Loomis and R. W. Wood, Phys. Rev. **32,** 223 (1928).

structure of the individual bands, which was verified by applying the combination principle. As was to be expected for a symmetrical molecule, the

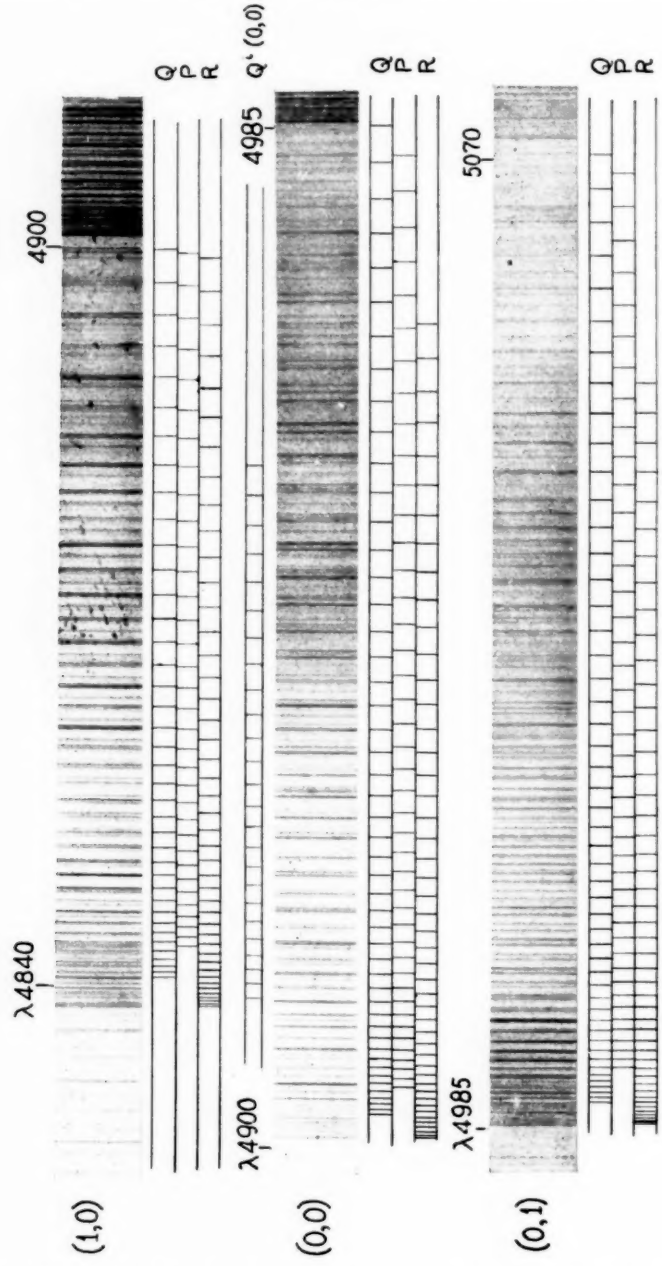

Fig. 1. Three bands of the blue-green system. Length of absorbing column 45 cm, $T = 630°C$. Second order of the 15 ft. grating.

intensities of successive lines showed a definite alternation. The alternation factor was estimated as between 1.20:1 and 1.33:1, but for reasons given be-

low the estimate was low. The vibrational isotope effect was also detected.[2] Li has isotopes of masses 6 and 7 in the proportion of about 1:16 (atomic weight 6.94). Besides the strong bands due to Li^7Li^7, two weaker systems should be present, due to Li^6Li^7 and Li^6Li^6, having respectively intensities 1/7.8 and 1/245 that of the strong system. The three most favorably placed band heads of the Li^6Li^7 system were observed. Measurements of heads are difficult in this case, especially at high temperatures, because the head occurs at a very low rotational quantum number. More satisfactory evidence of the isotope effect comes from a study of the rotational effect in the (0, 0) band the results of which will be given in the following section.

Near the completion of our work, two articles by Wurm[4,5] appeared, dealing with the blue-green and red systems of Li_2. The agreement of his analysis of the blue-green system with our unpublished results is excellent, not only in the wave-length data, but also in the quantum interpretation and in the resulting molecular constants. In point of self-consistency, our data seem nearly as accurate as those of Wurm, although obtained with somewhat lower dispersion (second order of a 15-ft. grating). This circumstance may be partly due to somewhat more favorable experimental conditions in our case, such as accurate control of the temperature of the electrically heated absorption tube. The spectra obtained in the present work, part of which are shown in Fig. 1, are undoubtedly less confused by the structure of faint underlying bands, since Wurm was only able to analyse the (0, 0) and (1,0) bands. We have been able to identify the branches of the (0, 1) band without difficulty, thus permitting a check on the combination differences in the lower, as well as in the upper state. Agreements in both states are required to be absolutely certain of a correct analysis.

Isotope Effect

Vibrational terms. From measurements of the heads of the blue-green bands an equation for the vibrational structure was derived,[1] which agreed well with that previously given by Wurm.[4] By suitably weighting the two sets of data, we have adopted the following equation for heads:

$$\nu_h = 20,398.40 + 267.3v' - 3.1v'^2 - 347.4v'' + 2.5v''^2, \qquad (1)$$

where v is the true vibrational quantum number, $v = 0, 1, 2 \cdots$, formerly called n. In seeking evidence for the vibrational isotope effect, it was apparent that the faintest (Li^6Li^6) system could not be detected, due to the complexity of the spectrum, and to the fact that few of the heads are pronounced. On a low-dispersion spectrogram, taken with a carefully adjusted vapor density, it was, however, possible to find the Li^6Li^7 heads of the (2, 0) and (3, 0) bands, the measured isotope shifts being 4.5 and 6.4A toward the

[4] K. Wurm, Zeits. f. Physik **58,** 562 (1929). We had unfortunately overlooked the preliminary notice of this work, (Naturwissenschaften **48,** 1028 (1928)), in which a vibrational analysis of the blue-green system is given, and an equation for heads which is in close agreement with that independently derived by us (Ref. 1). Alternation of intensities is also mentioned, but the rotational analysis had not been done.

[5] K. Wurm, Zeits. f. Physik **59,** 35 (1929).

violet, with a possible error of several tenths of a cm^{-1}. The theoretical shifts are most easily found by the following formula.[6] Denoting by a superscript i quantities appropriate to the Li^6Li^7 bands, this may be written

$$\nu_0{}^i-\nu_0=(\rho-1)(v'+\tfrac{1}{2})\omega_v'-(\rho-1)(v''+\tfrac{1}{2})\omega_v'' \tag{2}$$

where $\rho=(\mu/\mu^i)^{1/2}=1.040833$. From Eq. (1) we have

$$\omega_v'=\omega_e'-2x_e'\omega_e'(v'+\tfrac{1}{2})=270.4-2\times3.1(v'+\tfrac{1}{2});\ \omega_v''=349.9-2\times2.5(v''+\tfrac{1}{2}),$$

assuming that the coefficients apply equally well to band origins. This is justified here because the heads are at a small and nearly constant distance from the origins. The computed shifts in the above two cases are 4.3 and 6.3A, respectively. The (1, 0) isotope head is too close to the main band to be resolved with the prism spectrograph, but on a first order grating plate the attendant (1, 0) head could be measured with difficulty. The observed and calculated shifts in this case were 2.06 and 2.08A. On the red side of the system-origin, the fainter bands are entirely concealed by the Li^7Li^7 bands.

Rotational terms. In identifying the individual lines of the (0, 0) isotope band, more accurate and complete rotational constants of the strong system than those given by Wurm were required. We have therefore made an independent evaluation of these from our data. The wave-numbers of the rotational lines of the (0, 0) and (1, 0) band agree very well with Wurm's published data, although there is a small, nearly constant, discrepancy amounting to about 0.1 cm^{-1} on the average, our values being higher. Measurements of these bands are therefore omitted here, although the constants obtained from them are tabulated below. Table I gives wave-numbers in vacuum for the (0, 1) band, which was not analysed by Wurm, and also shows the agreement of the resulting term-differences, Δ_2F_0', with his values from the (0, 0) band.

In the calculation of rotational constants, we have assumed the following expressions for the rotational energy:

$$\begin{aligned}&{}^1\Sigma\colon F(K)=B''K(K+1)+D''\,[K(K+1)]^2+F''[K(K+1)]^3\\&{}^1\Pi\colon F(K)=B'[K(K+1)-1]+D'[K(K+1)-1]^2+F'[K(K+1)-1]^3.\end{aligned} \tag{3}$$

The observed rotational term-differences definitely require the F term, as is evident from Fig. 3 of Wurm,[4] where it was not taken into account. With the above term formulation, the $R-P$ differences should be given by

$$\Delta_2F(K)=4BK+8DK^3+12FK^5, \tag{4}$$

in which some negligible terms have been omitted. By means of the relations

$$D_e=-\frac{4B_e{}^3}{\omega_e{}^2};\quad F_e=\frac{D_e{}^3}{B_e}\left(2-\frac{\alpha\omega_e}{6B_e}\right);$$

[6] The general equation for the vibrational isotope effect has recently been considered by Birge (unpublished work). A sufficiently accurate approximation, in the present case, is given by the formula quoted, a form already used by Patkowski and Curtis, Trans. Farad. Soc. **25,** 725 (1929).

TABLE I. *Absorption lines and combination differences of the (0, 1) band.*

K	$R(K)$	$Q(K)$	$P(K)$	$\Delta_2F_1''(K)$	$\Delta_2F_0'(K)$	$\Delta_2F_0'(K)$*
6	20052.59	20044.63	20037.12		15.47	
7	051.81	042.90	034.78	20.42	17.03	
8	051.14	041.35	032.17	22.29	18.97	
9	050.36	039.37	029.52	24.83	20.84	
10	049.27	037.12	026.31	27.41	22.96	23.046
11	047.95	034.78	022.95	29.79	25.00	25.222
12	046.60	032.17	019.48	32.73	27.12	27.414
13	044.63	029.52	015.22	35.51	29.41	29.733
14	042.90	026.31	011.09	37.92	31.81	31.735
15	040.61	022.95	006.71	40.74	33.90	33.924
16	038.19	019.48	002.16	43.24	36.03	36.148
17	035.68	015.91	19997.37	45.83	38.31	38.350
18	032.73	012.00	992.36	48.54	40.37	40.431
19	029.52	007.81	987.14	51.02	42.38	42.570
20	026.31	003.47	981.71	53.54	44.60	44.649
21	022.95	19998.90	975.98	56.04	46.97	46.792
22	019.17	994.17	970.27	58.66	48.90	48.893
23	015.22	989.16	964.29	61.05	50.93	50.980
24	011.09	984.00	958.12	63.60	52.97	53.055
25	006.71	978.53	951.62	66.21	55.09	55.153
26	002.16	972.96	944.88	68.60	57.28	57.191
27	19997.37	967.17	938.11	71.26	59.26	59.245
28	992.36	961.06	930.90	73.65	61.46	61.310
29	987.14	954.71	923.72	76.06	63.42	63.394
30	981.71	948.27	916.30	78.52	65.41	65.369
31	975.98	941.61	908.62	80.97	67.36	67.338
32	970.27	934.63	900.74	83.40	69.53	69.348
33	963.95	927.52	892.58	86.08	71.37	71.277
34	957.75	920.17	884.19	88.27	73.56	73.315
35	950.98	912.64	875.68	90.75	75.30	75.238
36	944.19	904.90	867.00	92.90	77.19	77.053
37	937.14	896.92	858.08	95.06	79.06	79.119
38	929.97	888.71	849.13	97.49	80.84	81.010
39	922.46	880.30	839.65	99.87	82.81	82.872
40	914.80	871.62	830.10	102.11	84.70	
41	906.86	862.83	820.35	104.45	86.51	
42	898.84	853.86	810.35	106.74	88.49	
43	890.52	844.54	800.12	108.96	90.40	
44	881.88	835.03	789.88	111.15	92.00	
45	873.06	825.47	779.37	113.24	93.69	
46	863.61	815.53	768.64	115.54	94.97	
47	854.87	805.38	757.52	117.03	97.35	
48	845.52	795.02	946.58	119.88	98.94	
49	835.70	784.61	734.99	121.93	100.71	
50	825.47	773.07	723.59		101.88	
51	815.53	762.81				
52	805.38	751.79				
53	795.02	740.31				
54		728.84				

* (0, 0) band, Wurm.

TABLE II. *Rotational constants of Li_2^7 molecule.**

	Normal State ($^1\Sigma$)		Excited State ($^1\Pi$)	
	(H. & J.)	(Wurm)	(H. & J.)	(Wurm)
B_0	0.66914 cm^{-1}	0.6694	0.55321	0.5532
D_0	-0.9952×10^{-8}	-0.9865×10^{-8}	-0.9531×10^{-8}	-0.9407×10^{-8}
F_e	1.535×10^{-10}	—	1.337×10^{-10}	—
α	0.00744	—	0.00804	0.0084
β	0.765×10^{-8}	—	-14.48×10^{-8}	-11.7×10^{-8}
I_e	41.12×10^{-40} g cm^2	—	49.66×10^{-40}	—
r_e	2.67×10^{-8} cm	—	2.93×10^{-8}	—

* The values of B apply only to P and R branches (cf. text).

$$\beta=\frac{\alpha^2}{6\omega_e}+\frac{20\alpha B_e^2-32x_eB_e^3}{\omega_e^2};$$

$$B_v=B_0-\alpha v=B_e-\alpha(v+\tfrac{1}{2})\ ;\ D_v=D_e+\beta(v+\tfrac{1}{2})\ ;\ F_v\cong F_e\ ,$$

we have solved Eqs. (4) for the four states $v'=0, 1; v''=0, 1$, by a well-known procedure[7] involving a number of successive approximations. In this calculation, the vibrational constants from Eq. (1) were used; $\omega_e'=270.4$, $\omega_e''=349.9$, $x_e'=1.146\times10^{-2}$, $x_e''=0.7145\times10^{-2}$. Table II gives the final constants and a comparison with their values as found by Wurm.

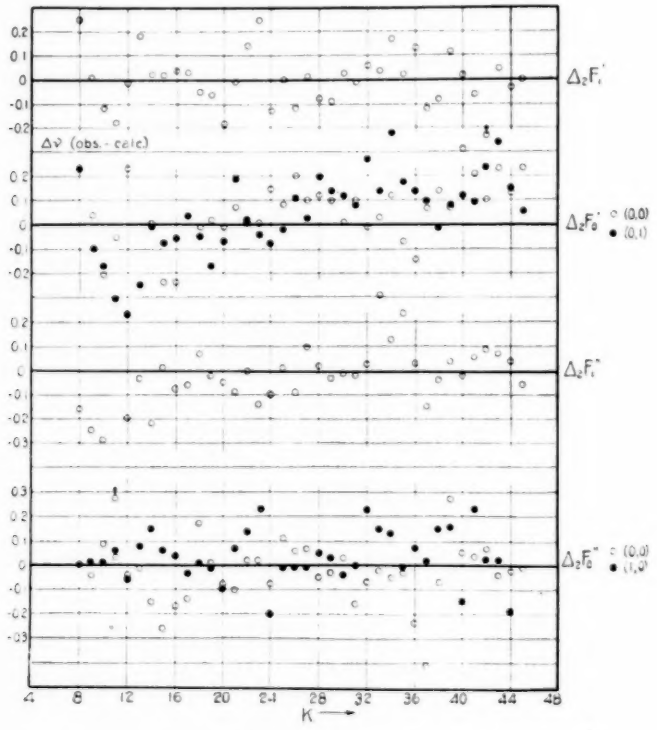

Fig. 2. Deviations (obs-calc) of all rotational term-differences from their values as given by Eq. (4).

Fig. 2 gives the residuals of the available term-differences from those calculated by Eqs. (4) using the above constants. The small linear trend which appears in the Δ_2F_0' residuals indicates the necessity for a small constant term in the true expression for Δ_2F. Such a "secondary ρ" term is justified theoretically, but was not used here since the error is small.

As is expected in a $^1\Pi$ state, the Λ-type doubling of rotational terms causes a small combination defect to appear when an attempt is made to obtain Δ_1F values by combinations with the Q branch. This doubling is proportional[4] to $(K+\frac{1}{2})^2$ and hence the initial terms of the Q branch may also be represented by Eq. (3), using a slightly smaller value of B. Wurm has found

[7] Method 3 of Birge, "Molecular Spectra in Gases," pp. 173–5.

this difference for the (0, 0) band to be $B_B' - B_A' = 0.00018$, and since our data on the combination defect are in essential agreement with his, we have adopted $B_0' = 0.55303$ for the Q branch.

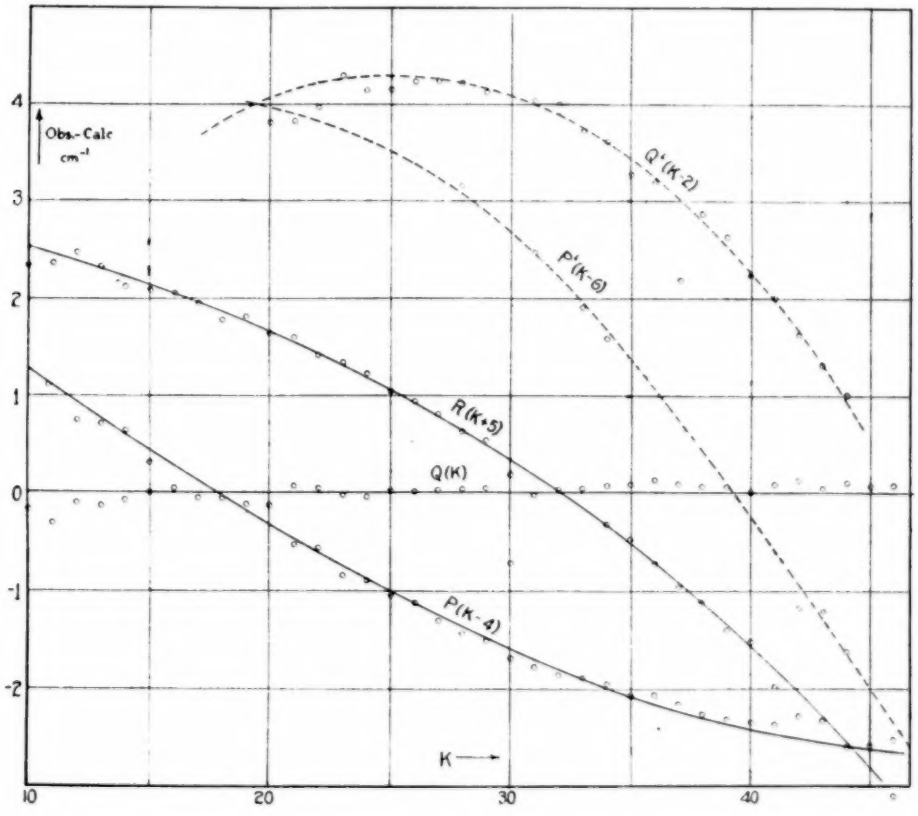

Fig. 3. Differences in wave-numbers of all lines of the (0, 0) band from the calculated Q lines. Solid lines, theoretical values from Eqs. (5); dotted lines, Q and P branches of the (0, 0) isotope band, from Eqs. (6).

A rigorous test of the accuracy of these constants is obtained by finding how well the observed *wave-numbers* of the P, Q and R branches are reproduced by the theoretical formulas:

$$\begin{aligned} R(K) &= \nu_0 - \tfrac{1}{4}C_B + 2B_B'(K+\tfrac{1}{2}) + (C_B + 4D')(K+\tfrac{1}{2})^2 + 4D'(K+\tfrac{1}{2})^3 \\ &\quad + (E+12F')(K+\tfrac{1}{2})^4 + 6F'(K+\tfrac{1}{2})^5 + G(K+\tfrac{1}{2})^6, \\ P(K) &= \nu_0 - \tfrac{1}{4}C_B - 2B_B'(K+\tfrac{1}{2}) + (C_B + 4D')(K+\tfrac{1}{2})^2 - 4D'(K+\tfrac{1}{2})^3 \\ &\quad + (E+12F')(K+\tfrac{1}{2})^4 - 6F'(K+\tfrac{1}{2})^5 + G(K+\tfrac{1}{2})^6, \\ Q(K) &= \nu_0 - B_A' - \tfrac{1}{4}C_A + (C_A - 2D')(K+\tfrac{1}{2})^2 + E(K+\tfrac{1}{2})^4 + G(K+\tfrac{1}{2})^6, \end{aligned} \tag{5}$$

where $C_A = B_A' - B''$, $C_B = B_B' - B''$, $E = D' - D''$ and $G = F' - F''$. Since the origin ν_0, is as yet undetermined, this amounts to testing the constancy of ν_0 as computed from the various lines. We find small trends of the order of 0.3

cm,$^{-1}$ and have taken 20,395.96 as the best average. To show the results of the calculation of wave-numbers of the lines by Eqs. (5), it is convenient to use a graphical method due to Loomis and Wood.[3] For this, a plot is made of the differences of every measured line in the band from the calculated values of the Q lines. Since the line series in bands of this kind run nearly parallel, the P and R branches also show on the diagram as series of points lying on a smooth curve. In Fig. 3 is given such a graph for the (0, 0) band. The two solid curves represent the differences of the *calculated* R and P lines from the adjacent Q lines. The agreement is as close as can be expected. This method of plotting was first used in identifying the branches of the (0, 0) band. It was then found that a number of lines were not accounted for as P, Q or R lines,

TABLE III. *Comparison of calculated and observed wave-numbers for the Q branches of the Li^7Li^7 and Li^6Li^7 (0, 0) bands.*

K	$Q(K)$ calc	$Q(K)$ obs	$Q^i(K)$ calc	$Q^i(K)$ obs
6	20390.53	20390.42		
7	388.91	388.80		
8	387.05	386.98		
9	384.96	384.96		
10	382.64	382.47		
11	380.09	379.78		
12	377.31	377.20		
13	374.29	374.15		
14	371.05	370.97		
15	367.57	367.56		
16	363.86	363.90		
17	359.92	359.86		
18	355.75	355.69	20350.76	20350.52
19	351.35	351.22	346.00	345.62
20	346.72	346.58	340.98	340.72
21	341.86	341.92	335.72	335.73
22	336.76	336.80	330.20	330.03
23	331.44	331.41	324.44	324.26
24	325.89	325.84	318.42	318.32
25	320.11	320.12	312.16	312.08
26	314.10	314.10	305.66	305.61
27	307.86	307.88	298.90	298.82
28	301.40	301.43	291.90	
29	294.70	294.74	284.64	284.66
30	287.78	287.96	277.15	277.25
31	280.62	280.60	269.40	269.35
32	273.25	273.28	261.41	261.41
33	265.64	265.68	253.18	253.01
34	257.80	257.87	244.69	244.67
35	249.74	249.82	235.96	
36	241.47	241.60	226.99	227.07
37	232.94	233.03	217.77	217.86
38	224.20	224.27	208.31	208.27
39	215.23	215.29	198.60	198.62
40	206.04	206.05	188.65	188.59
41	196.62	196.71	178.45	178.42
42	186.97	187.11	168.01	168.01
43	177.10	177.15		
44	167.01	167.12		
45	156.69	156.76		
46	146.15	146.24		
47	135.38	135.34		
48	124.39	124.36		
49	113.18	113.05		
50	101.74	101.65		

and, in fact, a number formed a distinct fourth series, with indications of a fifth. The explanation of these extra branches appears when the positions of the isotope lines of the (0, 0) band of Li^6Li^7 are determined by the theory of the isotope effect. The origin $\nu_0{}^i$, of this band is, from Eq. (2), 1.635 cm^{-1} lower in wave-number than that of the strong (0, 0) band. Assuming, as is usual, a negligible electronic isotope effect, we may now compute all the lines of the fainter band. It is only necessary to multiply the coefficients of Eqs. (5) by the appropriate powers of ρ, and to insert the new origin. There results:

$$\begin{aligned}
R^i(K) &= \nu_0{}^i - \tfrac{1}{4}\rho^2\mathcal{C}_B + 2B_B{}'\rho^2(K+\tfrac{1}{2}) + (\rho^2\mathcal{C}_B + 4\rho^4 D')(K+\tfrac{1}{2})^2 + 4\rho^4 D'(K+\tfrac{1}{2})^3 \\
&\quad + (\rho^4 E + 12\rho^6 F')(K+\tfrac{1}{2})^4 + 6F'\rho^6(K+\tfrac{1}{2})^5 + \rho^6\mathcal{G}(K+\tfrac{1}{2})^6, \\
P^i(K) &= \nu_0{}^i - \tfrac{1}{4}\rho^2\mathcal{C}_B - 2B'_B\rho^2(K+\tfrac{1}{2}) + (\rho^2\mathcal{C}_B + 4\rho^4 D')(K+\tfrac{1}{2})^2 - 4\rho^4 D'(K+\tfrac{1}{2})^3 \quad (5') \\
&\quad + (\rho^4 E + 12\rho^6 F')(K+\tfrac{1}{2})^4 - 6F'\rho^6(K+\tfrac{1}{2})^5 + \rho^6\mathcal{G}(K+\tfrac{1}{2})^6, \\
Q^i(K) &= \nu^i{}_0 - \rho^2 B_A{}' - \tfrac{1}{4}\rho^2\mathcal{C}_A + (\rho^2\mathcal{C}_A - 2\rho^4 D')(K+\tfrac{1}{2})^2 + \rho^4 E(K+\tfrac{1}{2})^4 + \rho^6\mathcal{G}(K+\tfrac{1}{2})^6.
\end{aligned}$$

The calculated Q^i and P^i branches are shown in Fig. 3 to be in excellent agreement with the two anomalous series, although P^i is rather fragmentary, due to its faintness. With these isotope lines explained, only two measured lines in the (0, 0) band remain unaccounted for, and one perhaps belongs to the R^i branch. This constitutes probably the most exacting test of the theory of the isotope effect yet applied. The numerical accuracy of the agreement appears in Table III. This is within the error of the calculation, and hence discrepancies cannot be taken as indicating that the atomic weights of Li^6 and Li^7 do not differ by integers.

Further confirmation of the isotope character of these lines is found in their failure to show alternating intensities, as discussed below.

Alternating Intensities

The alternation of the intensities of successive lines in each branch already established by the writers,[1] and by Wurm,[4] is of special interest, since the alternation ratio gives a measure of the spin of the Li nucleus.[8] To determine the latter, a quantitative measure of the ratio is required. This is particularly difficult in the present case, due largely to the many erratic fluctuations resulting from superpositions with faint underlying structure. There is also the difficulty, at least with our experimental arrangements, that neither the density of vapor nor length of the absorbing column can be found accurately, so that calculations of the absorption coefficients cannot be made, even though the intensities of the absorption lines themselves be correctly evaluated. It was at first thought that the vapor density was low enough for the observed intensities of absorption to be proportional to absorption coefficients, and a preliminary estimate of the ratio was made with this assumption. Density curves were obtained with the Zeiss-Koch recording microphotometer. An example of these curves is given in Fig. 4. In each branch of the (0, 0) band, the average electrometer deflection (background to line center) for the stronger set of lines, those with odd K'', was compared with

[8] For a review of this theory see R. S. Mulliken, Trans. Faraday Soc. **25**, 634 (1929).

the average deflection for the weaker set. The ratio of these gave 1.2:1. Using the usual law relating densities to intensities, the alternation ratio was estimated as lying between 1.2 and 1.33. Uncertainty in the estimated contrast factor, γ, allowed considerable latitude in this result. Upon repeating the microphotometer curves with a better spectrogram, it was found that, by

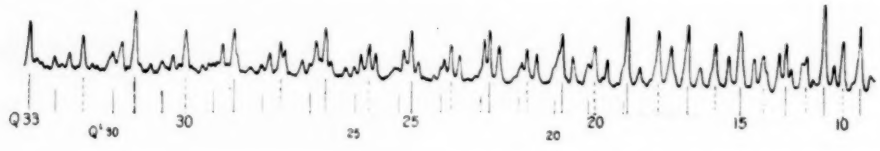

Fig. 4. Microphotometric trace (retouched) of part of the (0, 0) band, showing alternation of intensity in the Q branch of the stronger (Li^7Li^7) band. No alternation is apparent in the weaker branch, Q^i, due to Li^6Li^7.

plotting the electrometer throws for a given branch two fairly good curves were obtained, corresponding to the stronger and weaker sets, as shown in Fig. 5. A number of values lie definitely above the general run, and many of these lines are shown by the structure analysis to be blended with other lines of the band. Neglecting these, and giving the smaller values more weight

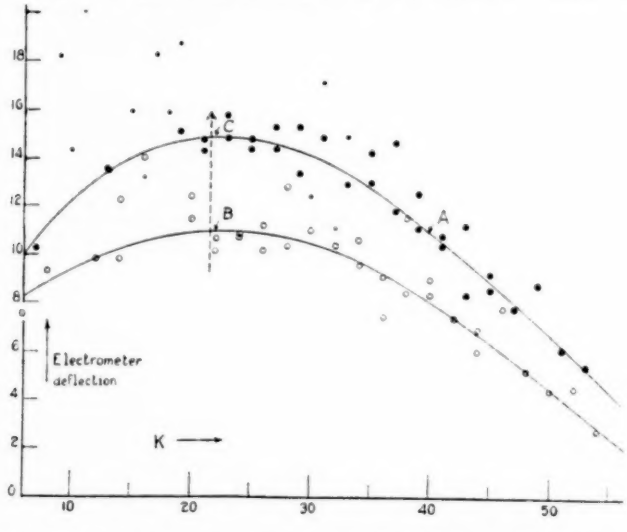

Fig. 5. Height of peaks on microphotometer curves for the Q branches of the (0, 0) and (1, 0) bands as a function of K. To render the two sets of data comparable, that for the (1, 0) band has been multiplied throughout by 0.84. Dots represent the stronger set of lines (K odd) and circles the weaker (K even). Lines known from the analysis to be blends are indicated by small dots or circles. The arrow indicates the theoretical intensity maximum, from Eq. (7). The significance of points A, B and C is discussed in the text.

in drawing the curves, satisfactory curves could be obtained for the Q branches of the three bands studied. The mean ratio of the deflections now becomes about 1.4:1. It will be seen that failure to take into account the evident superpositions tended to render our earlier estimate of the ratio too low.

A new method has now been applied which renders unnecessary the evaluation of absorption coefficients, or determination of γ, since it rests purely on the *equality* of certain intensities. Thus, in Fig. 5, we first determine the value of K for the point A, at which the deflections for the stronger set have fallen to that of the maximum value, B, in the weaker set. Since the blackening is the same at A and B, the intensities are equal at these points. We may then calculate, using the well-established theoretical formulas for intensities in $^1\Sigma - {}^1\Pi$ bands,[9] the ratio of intensities of two lines having the K values of points A and B, which ratio is then the required one, becuase the intensity ratio of points C to A equals that of C to B.

The intensity distribution in the Q branch of a band with $\Lambda' - \Lambda'' = +1$ is given, according to Mulliken's formulas,[9] by

$$I_Q = [2A(K+\tfrac{1}{2})(K+\Lambda')(K+1-\Lambda')/K(K+1)]e^{-E/kT}$$

or, when $\Lambda' = 1$

$$I_Q = A(2K+1)e^{-E/kT}. \tag{6}$$

Since we are dealing with absorption, $E = F''(K)$. This formula has been shown[9] to be in agreement with experimental data in a number of cases. The corresponding equations for the P and R branches were not of use for the purpose in hand, since the data for these branches, which are roughly half as intense as the Q branch, are not as complete or as consistent. Appreciable deviations of experiment from theory have also been found,[9] particularly in the case of the P branch. It therefore seems best to restrict ourselves to the Q branches, and to evaluate the alternation ratio from the curves of Fig. 5.

First we may show that Eq. (6) is in agreement with the observed K value of the maximum intensity. Differentiating, and equating to zero:

$$\frac{dI_Q}{dK} = 2Ae^{-E/kT} + A(2K+1)e^{-E/kT}\frac{d}{dK}\left(-\frac{E}{kT}\right) = 0$$

whence we find, inserting for E its value $B''[K(K+1)] + D''[K(K+1)]^2$ that, for the intensity maximum,

$$2B''(K+\tfrac{1}{2})^2 + 4D''(K+\tfrac{1}{2})^4 = kT. \tag{7}$$

The temperature of the absorption tube was measured by a thermocouple in direct contact with the heavy Ni tube which was covered with asbestos and electrically heated from the outside. For the plate used in this work $T = 630° \pm 10°\text{C} = 903°K$. Solving Eq. (7), using the B_0'' and D_0'' from Table II, it is found that, for the maximum of intensity, $K = 21.5$. Fig. 5 shows that this is in good agreement with the observed value.

Such a check on the correctness of the theory lends more confidence to the application of the method for determining the alternation ratio outlined above. From Eq. (6) we obtain the ratio of any two lines of the Q branch,

$$I_{Q(K_1)}/I_{Q(K_2)} = \frac{K_1+\tfrac{1}{2}}{K_2+\tfrac{1}{2}}e^{(E_2-E_1)/kT}. \tag{9}$$

[9] R. S. Mulliken, Phys. Rev. **29**, 391 (1927).

The stronger lines of the Q branch become equal to the maximum of the weaker set at $K=40$ (point A, Fig. 5). The ratio of intensities at C and A then becomes, from Eq. (6),

$$I_{Q(22)}/I_{Q(40)}=\frac{22+\frac{1}{2}}{40+\frac{1}{2}}\exp\left[\frac{1070.62-336.04}{903\times 0.698}\right]=1.78.$$

A similar evaluation from the (0, 1) band with much less reliable data, and fewer points, gave 1.50. The limit of accuracy of these figures is determined principally by the accuracy with which the curves can be drawn. It is found, however, that the highest possible value for the ratio, corresponding to a reasonable fit with the observed points is 2.0, and the lowest 1.6. The result is also rather sensitive to the value of T assumed. A change of T by 10° changes the ratio by 0.02. We obtained consistent readings of the temperature with the Pt-Pt, Rh thermocouple in various positions along the length of the tube, and it was standardized at the melting point of antimony, 630.5° C. A certain portion of the vapor near the water-cooled ends of the tube must of course have been at a lower temperature, but the vapor density decreases rapidly at this temperature, the absorption with the tube at 580°C being negligible.[10] Hence the effects of the cooler ends should not be great.

According to the theory of alternating intensities in band spectra,[8] only certain definite values of the alternation ratio are possible. Denoting by i the angular momentum of the Li nucleus in units $h/2\pi$, the statistical weights of successive rational levels contain a factor alternating in the ratio $(i+1)/i$. The nuclear spin, i, may in general be integral or half-intergal. In the neighborhood of the observed value we have the following possibilities:

$i=1$	$3/2$	2
Ratio 2:1	1.67:1	1.50:1

The value 1.67 is within the limit of error of our measurement, but the others are not excluded. In view of relations discussed below, however, they must be regarded as improbable. From eye estimate of intensities by Wurm,[4] the average ratio of successive lines is 1.7:1, and in the red bands[5] he estimates the factor to be 2:1.

These results therefore indicate the spin of the Li nucleus to be $3/2$ $h/2\pi$. This is in harmony with some recent generalizations[11] which have been drawn by considering all known values of i. For convenience the latter are collected in Table IV.

The conclusion of Heitler and Herzberg[12] that the spin of the electron is not effective in the nucleus, and that the addition of one proton adds or subtracts $\frac{1}{2}$ unit finds strong support in such a table. On this view, an integral value of i would not be expected for Li^7, nor for any atom with an odd number of protons. One is fairly sure that in Li^7 the α-particle configuration gives a resultant spin of zero; for the He nucleus it is proven by the absence of alter-

[10] Wurm, Ref. 4, estimates absorption to begin at 400°C. We were unable to detect any molecular absorption below 580°C.

[11] H. Schüler and H. Brück, Zeits. f. Physik **58,** 735 (1929).

[12] W. Heitler and G. Herzberg, Naturw. **17,** 673 (1929).

nate lines in the band spectrum that $i=0$. The probable value of 3/2 in our case may then be interpreted as due to the parallel orientation of the spins of the three remaining protons. It will be seen in Table IV that all atoms with an odd number of nuclear protons heretofore studied have yielded only values of $i=\frac{1}{2}$, 5/2, and 9/2, differing by 4/2. The possible significance of

TABLE IV.

Element	Number of nuclear		Nuclear spin $=i$	Determined from
	Protons	Electrons		
H	1	0	$\frac{1}{2}$	Band Spectra
He	4	2	0	" "
Li^7	7	4	3/2	" "
C^{12}	12	6	0	" "
N^{14}	14	7	1	" "
O^{16}	16	8	0	" "
F	19	10	$\frac{1}{2}$	" "
Na	23	12	>5/2	" "
Cl^{35}	35	18	5/2	" "
Mn	55	30	5/2	Hyperfine structure
Zn	64	34		
	66	36	0	Hyperfine structure
	68	38		Zeeman effect
	70	40		
Cd	110	62	0	
	111	63	$\frac{1}{2}$	
	112	64	0	Hyperfine structure
	113	65	$\frac{1}{2}$	
	114	66	0	
	116	68	0	
I	127	74	>5/2	Band spectra
La	139	82	5/2	Hyperfine structure
Pr	141	82	5/2	" "
Tl	205	124	$\frac{1}{2}$	" "
Bi	209	126	9/2	Hyperfine structure Zeeman effect

this has been mentioned by White,[13] but it may be that the absence of intermediate values is due to the scarceness of data for the lighter elements. In a preliminary announcement of their work on the hyperfine structure of the Li II line λ5485, Schüler and Brück[11] state that the pattern can be completely explained on the assumption that $i=\frac{1}{2}$ for the Li^7 nucleus. It will be readily seen even upon visual inspection of the bands in Fig. 1, that the alternation ratio of 3:1 required by this is out of the question.

In conclusion, we may mention that a careful examination of the photometric curves has failed to reveal any consistent alternation in the intensities of the lines in the Q branch of the (0, 0) band due to the isotope molecule, Li^6Li^7. The ratio of the average height of the peaks for odd K to that of even K was 1.05:1, which means sensible equality when we are dealing with such faint lines. The absence of alternation is of course to be expected for a non-symmetrical molecule, and our result is similar to that obtained by Elliott[14] from his study of the Cl_2 bands.

[13] H. E. White, Phys. Rev. **34,** 1404 (1929).
[14] A. Elliott, Proc. Roy. Soc. **123A,** 629 (1929).

INTENSITY MEASUREMENTS IN THE ARC SPECTRUM OF THALLIUM*

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Abstract

Measurements were made by the photographic method of the ratio of the intensities of the lines $2p_2-2s$, $2p_1-2s$ in the arc spectrum with a current of 1.6 amp. using alloys of lead and thallium in varying proportions. The ratio increased with decreasing concentration of thallium reaching a limit at about 0.01 per cent, the effects of absorption being negligible at this stage. The limiting value for $\overline{a_2^2}/\overline{a_1^2}$ is 0.388, where $I=a^2\nu^4$. Commercial lead was found to have a considerable thallium content making it necessary to use chemically pure lead. Measurements of the ratios of intensities of doublets in the principal series $2s-mp_1$, $2s-mp_2$ were made for $m=4$, 5, 6 and 7 the values obtained for $\overline{a_1^2}/\overline{a_2^2}$ being respectively 4.5, 5.7, 6.4 and 7 of which the last two are very uncertain. The values were found to be independent of concentration of thallium and of the current over a restricted range of tests. The fraction of light transmitted through an antimony film reducer was found to vary with wave-length as follows: λ, 6550, 0.270; λ, 5530, 0.243; λ, 5350, 0.243; λ, 4890, 0.175; λ, 3780, 0.093. The diffraction effects recorded by Shenstone were observed and photometer diagrams are given in illustration.

A CONSIDERABLE amount of work has been done by several investigators on the measurement of intensities of doublets in the arc spectra of the alkalies and a number of interesting and important results have been obtained such as the relations between the ratio of intensities in the doublet, the effective quantum number and the atomic number, found by Sambursky.[1] It is therefore a matter of interest that similar observations should be made with another metal giving doublets but belonging to a different group and for this reason this investigation on the arc spectrum of thallium was commenced.

The method employed was the photographic one developed by Professor Ornstein and in general use in the Physical Laboratory in Utrecht.[2] A Hilger quartz spectrograph, type E-2, was used with photogaphic plates of several kinds, namely, Ilford Iso-Zenith, Ortho-Chromatic, Pan-Chromatic and Soft Gradation Pan-Chromatic according to the spectral region being examined.

Density marks were taken on all the plates; these consisted of continuous spectra from a quartz tungsten band lamp, the varying slit method being employed. For the calibration of the lamp and the calculation of the spectral distribution of the energy for the various currents used I am indebted to Mr.D Vermeulen. With most of the plates for each exposure, both of arc and continuous spectra, two intensities were obtained by means of a reducer placed

* Communication from the Physical Laboratory, the State University of Utrecht.

[1] S. Sambursky, Zeits. f. Physik, **49**, 731 (1928).

[2] L. S. Ornstein, Proc. Phys. Soc. London **37**, 334 (1925).

in front of the slit of the spectrometer. This consisted of a quartz plate on half of one surface of which a thin film of antimony had been deposited by evaporation in vacuum. By this means it was possible to overcome the difficulty arising from the very great differences between the intensities of the lines on the plates found with some of the doublets examined though in the case of each pair, by selection of suitable times of exposure and the use of absorbing screens, many comparisons were made using the same half of the spectrum for both lines so that errors due to inequalitities in the comparatively narrow spectrometer slit were negligible. The two intensities were used mainly to extend the range of calibration of the plate and as a means of checking the trustworthiness of the work by the parallelism of the two graphs obtained when the photometer records of the density marks were plotted against the logarithms of the slit widths. In all cases the transmission of the antimony screen was determined photographically from the distance between the two curves thus obtained so that the values are free from any error which might be introduced in a direct determination with a somewhat different optical system.

Several of the lines examined, in particular that of wave-length 5350A occur in a region where the sensitiveness of the plate changes to a marked degree for a very small spectral displacement, and special care was needed in the calibration of the plates with the photometer in these cases. It was found that when the plateholder was moved up and down in the camera its path was slightly curved so that if the plate were aligned in the photometer in such a way that the images of a given line in spectra at the top and bottom of the plate passed across the middle of the thermopile slit, the images of corresponding lines in spectra in the middle of the plate were appreciably displaced from this position. The path of the plateholder was, however, reproduced with sufficient exactness when the up and down motion was repeated and errors arising from this were minimized by taking many arc spectra on the plate with not more than two continuous spectra between successive arc spectra. By aligning the plate in the photometer for each successive pair of arc spectra satisfactory records were obtained for the intervening continuous spectra, as was shown by the two graphs being continuous and parallel.

THE DOUBLET $2p_1-2s$, $2p_2-2s$.

The first pairs of lines examined was the first doublet in the Sharp series, $2p_1-2s$, $2p_2-2s$ of wave-lengths 5350. 46 and 3775.72. Some difficulty was experienced with these lines because of the feature of plate sensitiveness discussed above and because of the very great disparity between the ratio of intensities of the two lines on the plates and the ratio of the intensities of the continuous spectrum in the same regions. In the final cases with the tungsten band at a temperature of 2750°K the slit widths making the continuous spectrum equivalent to the lines were in the ratio of 40:1, that for the ultra-violet line being the greater. It was found convenient to use in the path of the light a screen consisting of a glass cell containing a dilute aqueous solution of potassium ferrocyanide, which absorbed the ultra-violet to a much greater

extent than the green though of course the same occurred in the case of the continuous spectrum. The fact that the transmission of the antimony reducer was more than 2.5 times as great for the green as for the ultra-violet line was also helpful.

These two lines are strongly reversed when the intensity is at all great and to make a satisfactory determination of the ratio of intensities it was necessary to obtain conditions under which the absorption causing this reversal does not occur.

In the first trials an arc was used between poles made of an alloy of lead and thallium; these were rods, 12 mm in diameter forced into slightly smaller hollows in heavy copper rods. The relative intensities of the two lines were measured using alloys with several different concentrations of thallium it being expected that when the proportion of thallium was reduced the effect of absorption would become less because of the smaller amount of thallium vapor in the arc so that the true value of the ratio would be approached. The current was kept at the same value, 1.5 to 1.6 amp. throughout, the supply voltage being 440. With decreasing concentration it was found that the ratio of intensity of the ultra-violet to the green line increased, this being explained by the absorption being greater in the case of the line of shorter wave-length so that this line should gain relatively when the conditions favored decreased absorption. With the strongest concentrations used, probably 2 or 3 percent thallium, a wide range of values was obtained the explanation of which is the lack of homogeneity of the poles, there being comparatively large regions relatively rich or poor in thallium, so that the arc at different times corresponded with alloys of different concentrations. With smaller concentrations of thallium more regular results were obtained, due probably, in part to a more nearly homogeneous alloy, and in part to the fact that the exposures were longer, minutes instead of seconds, so that various parts of the pole surfaces were in turn the source of the vapor in the arc and a more uniform average value was obtained.

The ratio of intensities was found still to increase with extremely small concentrations and, as it was found at this stage that the commercial lead used in making the alloys contained an appreciable amount of thallium, it became uncertain whether even the dilution in this lead without the addition of any thallium would give the limiting ratio sought. Other specimens of lead examined were found to contain thallium but some "chemically pure" lead was obtained in which the thallium content, if any, was certainly very much smaller so that fresh trials were made in which this lead was used to make the alloys. The results of the experiments with the impure lead are shown in the upper part of Fig. 1, the ordinates being proportional to the ratio of intensities (ultra-violet to green) and the abscissas to the logarithms of the concentration of thallium on an arbitrary scale. The latter are certainly incorrect being based on the assumption that the lead was free from thallium.

As in the first method of producing the arc there was a considerable loss of material through the melting of the poles a new method had to be employed

with the chemically pure lead, especially as it was clear that very small concentrations of thallium would be required, and therefore very long exposures. A Pfund type of arc was used with copper poles, the alloy being placed in a cup shaped hollow on the lower one. The current had the same value as in the earlier experiments, 1.6 amp. Generally it was not found possible to maintain the arc between the upper pole and the alloy for a long time; either the arc would go out or else run to the side of the lower pole. When this occurred the light was at once cut off and the copper cup scraped free of the layer of lead oxide formed on it and a fresh supply of alloy introduced when the arc could be re-started. In this way spectra were obtained in which the copper lines were relatively weak. When the arc passed from copper to copper the thallium lines were still present but of course corresponded with a much smaller concentration of thallium than that in the alloy under examination. It was much easier to maintain a larger current in this way but the small current seemed more likely to give the limiting value for the ratio of intensities.

By this method of experiment consistent results were obtained with various concentrations of thallium and it was found that a point was reached at which a reduction in the proportion of thallium gave no further increase in the ratio of intensities. Several values with very much smaller concentrations confirmed this.

TABLE I. *Ratio* $\overline{a_2^2}/\overline{a_1^2}$ *for the doublet* $= 2p_2 - 2s$, $2p_1 - 2s$ *for various concentrations of thallium.*

Percentage of thallium	Number of observations	Mean value of $\overline{a_2^2}/\overline{a_1^2}$	Mean error
0.072	5	0.093	0.009
0.040	3	0.236	0.040
0.087	10	0.372	0.045
0.0051	2	0.395	0.018
0.00143	1	0.382	
0.00024	2	0.388	0.032

The results are given in Table I and shown graphically in the lower part of Fig. 1. The alloys of lower concentration were made by melting stronger ones with lead and the actual numerical values of the concentrations may not be correct because the lead might contain an amount of thallium comparable with that intended in the weakest concentrations and because in melting the product was always less than the sum of the constituents used there being always some dross in which the metals might be in very different proportions from those in which they are placed in the crucible. In the case of the larger concentrations the errors cannot be great and that the concentration became successively less is shown by the fact that the time needed for satisfactory intensities of the lines became greater for each dilution so that there is no room for doubt that the limiting value was attained. On account of the long exposures required with the smallest concentrations—of the order of an hour—the effect of the "continuous spectrum" became relatively great and the value is not very accurate. On the other hand the others are trust-

worthy it being considered for example that the error in that for concentration 0.0087 percent is not more than 2 percent.

In Table I and Fig. 1 the ratio $\overline{a_2^2}/\overline{a_1^2}$ is obtained from the ratio of intensities I_2/I_1 by multiplying by the factor λ_2^4/λ_1^4, a_1 and a_2 being the amplitudes of the virtual resonators given by the equation $I=a^2\nu^4$.

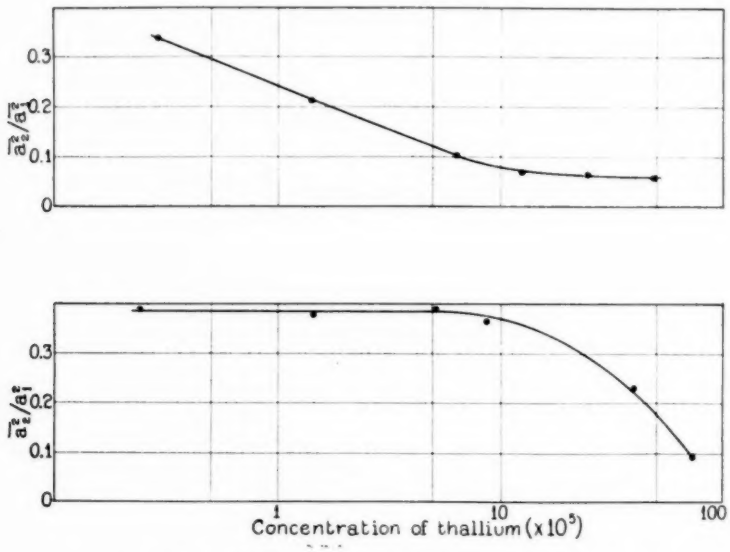

Fig. 1. Values of $\overline{a_2^2}/\overline{a_1^2}$ as a function of thallium concentration.

The values of I_2/I_1 were of course obtained from the ratio determined from the photometer records multiplied by factors for the relative intensities of the lamp radiation at the two regions and for the relative dispersion of the spectrometer.

The limiting values found are

$$I_2/I_1=1.56\ ;\quad \overline{a_2^2}/\overline{a_1^2}=0.388$$

where the suffixes 1 and 2 refer respectively to the line of longer and shorter wave-length.

The last column of Table I gives the mean of the differences between the individual observations and the mean.

The Principle Series $2s-mp_1$, $2s-mp_2$.

Measurements were next made of several doublets in this series. The first, occurring in the infra-red could not be attacked by this method but trustworthy determinations were made in the case of the second and third doublets and values were obtained for the fourth and fifth which must be taken simply as indicating the order of the true values as large errors may have been made in their measurement.

The problem is simpler than that of the lines first examined because the separation of the doublets is less and because the effects of absorption are negligible. The Pfund arc was employed, generally with pure thallium though some determinations were made with a lead alloy of 50 percent thallium, and some with a current of 3.5 amp. instead of 1.6, used in most of the work. No appreciable differences were found in the results, justifying the view that the effects of absorption are negligible. That no error was introduced by copper lines in the proximity of lines examined in the case of the first two doublets measured was shown by obtaining spectra of a copper arc with a current of the same value, 1.6 amp., with exposures longer than any used in the measurements. Such lines did not appear, though with a copper arc of 6 amp. copper lines in the neighborhood of the first pair, 6700-6500, were recorded.

The results obtained with these two doublets, recorded below in Table II, show the ratio of intensities, that of shorter wave-length to that of longer, to be distinctly greater for the pair of greater quantum number and attempts were made to obtain values for doublets of higher order. As much longer exposures were needed with these, difficulties arose from the greater continous spectrum and from the presence of neighboring copper lines not obtained before with the relatively short exposures. Spectra were obtained using poles of carbon and other materials in the hope of obtaining better results. In several cases, mostly with the copper arc, the conditions were such that both lines of one or both doublets were obtained free from appreciable reinforcement from neighboring lines of other elements and of sufficient intensity to allow measurements to be made.

TABLE II. *Ratio* $\overline{a_1^2}/\overline{a_2^2}$ *for doublets in the principal series* $2s-mp_1$, $2s-mp_2$.

m	Wave-lengths	Number of observations	Mean value of $\overline{a_1^2}/\overline{a_2^2}$	Mean error
4	6549.77 6713.69	8	4.5	0.44
5	5527.90 5583.88	11	5.7	0.92
6	5109.47 5136.84	1	6.4	
7	4891.11 4906.3	3	7	1

The values obtained for the doublets in this series are given in Table II. The ratio of $\overline{a_1^2}/\overline{a_2^2}$ rises with the quantum number but in view of the possibility of large error in the last two values it is impossible to decide whether the values conform with the equation found by Sambursky[1] in the case of the alkalies, namely

$$I_1/I_2 = cn^a{}_{eff}$$

where n_{eff} is the effective quantum number.

As it was impossible for me to remain longer in Utrecht further work could not be done at this stage. It is my intention to continue this investigation on my return to Sydney.

Note 1. The fraction of light transmitted by the antimony screen was determined in the individul cases with an error not exceeding 2 percent. The values, however, were found to vary somewhat according to the part of the screen employed and as it was frequently removed and replaced between the taking of one plate and another a fairly wide range of values was obtained particularly for the shortest wave-length employed. The mean values obtained have some interest and are given in Table III.

TABLE III. *Transmission of antimony film.*

λ	fraction transmitted	λ	fraction transmitted
6549	0.270	4891	0.175
5527	0.243	3776	0.093
5350	0.243		

Note 2. In the first stage of the work there was in many of the photometer records of line 3776 an indication of a companion line on the red side as illustrated in Fig. 2 a. Further examination with altered conditions of the optical system showed that this was a diffraction effect and that similar effects were obtained with many of the intense lead lines. A lack of symmetry of the diffraction pattern in many cases and abnormal intensities of the

Fig. 2. Photometer records of line 3776 showing presence of secondary maxima, (a) obtained with wide spectrometer slit giving unsymmetrical pattern, (b) with narrow slit, nearly symmetrical.

fringes were observed similar to those recorded by Shenstone[3] whose paper came to hand while this work was in progress. In Fig. 2b is given a photometer record of line 3776 the spectrum being taken with a fine spectrometer slit. In this case the pattern is symmetrical and measurement of the displacements agree closely with those calculated from the ordinary theory.

In conclusion I wish to express my warm thanks to Professor Ornstein for giving me the opportunity, during my stay in Utrecht, of obtaining an intimate knowledge of the research methods used in his laboratory and in particular for his continued interest and help in this work.

[3] A. G. Shenstone, Phys. Rev. **34**, 726 (1929).

THE FREQUENCY OF OCCURRENCE OF THE DISINTEGRATIVE-SYNTHESIS OF OXYGEN 17 FROM NITROGEN 14 AND HELIUM

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ABSTRACT

By the use of a modified Wilson-Shimizu apparatus 39000 photographs were taken of the tracks of α-rays in nitrogen. The rays used were those from thorium C and C' as in earlier work in this laboratory. Two disintegrative syntheses were obtained of oxygen of mass 17 and isotopic number 1 by the attachment of the α-particle in each case to the nucleus of an atom of nitrogen. Evidence is presented which shows that the nitrogen atoms which are acted on in this way are in general those of mass 14 and isotopic number 0. The number of disintegrative syntheses per million α-tracks is 8, while the average of this and all other work gives 15. In this work the ratio of the number of inelastic to elastic collisions was smaller than in any earlier work, but this was due largely to the occurrence of an abnormally high number of elastic collisions.

INTRODUCTION

THE procedure now in use for the detection of the synthesis of a heavier atom from two lighter ones is that suggested and used by Harkins and Ryan.[1] They considered that if very fast α-particles were shot into a Wilson cloud-expansion chamber, and if a sufficiently large number of photographs were taken, the mechanism of any atomic disintegrations would be partly revealed. By the use of this method Harkins and Shadduck[2] found that two disintegrative syntheses of oxygen of mass 17 and isotopic number 1 were obtained by shooting about 250,000 α-rays of 8.6 cm range from thorium C′ through nitrogen gas. Although 135,000 tracks of 4.9 cm range were also obtained, the analysis of the forks indicates that only the long range particles were effective in producing disintegrative-syntheses.

This yield of eight such events per million long range tracks is very small, and Kirsch and Petterson consider that the number should be very much higher. While it is true that one or two hydrogen tracks might have escaped observation, it is improbable that this is the case, on account of the method of observation. The 39,000 photographs were projected on a screen, one at a time, usually with two observers present. Every negative which showed a deflection in an α-track was cut out from the film, whether the track of another atom was present or not. All films on which the forks were well defined were segregated, and particular attention was paid to the observation in the other photographs of those deflections which were not so clear, and in which there was any possibility of the occurrence of a disintegra-

[1] W. D. Harkins and R. W. Ryan, J. Am. Chem. Soc. **45**, 2095 (1923).
[2] W. D. Harkins and H. A. Shadduck, Proc. Nat. Acad. Sci. **2**, 707 (1926).

tion. A second observation of all of the film in order to find deflections which might have been missed earlier, was also made. Pettersson and Kirsch[3] consider that short range protons would be more likely to be missed than long range particles, such as are commonly found by the photographic method, but it is our opinion that they should be more easily seen, on account of the increase of ionization with decrease of speed of the particle, within the limits of the range of speed involved.

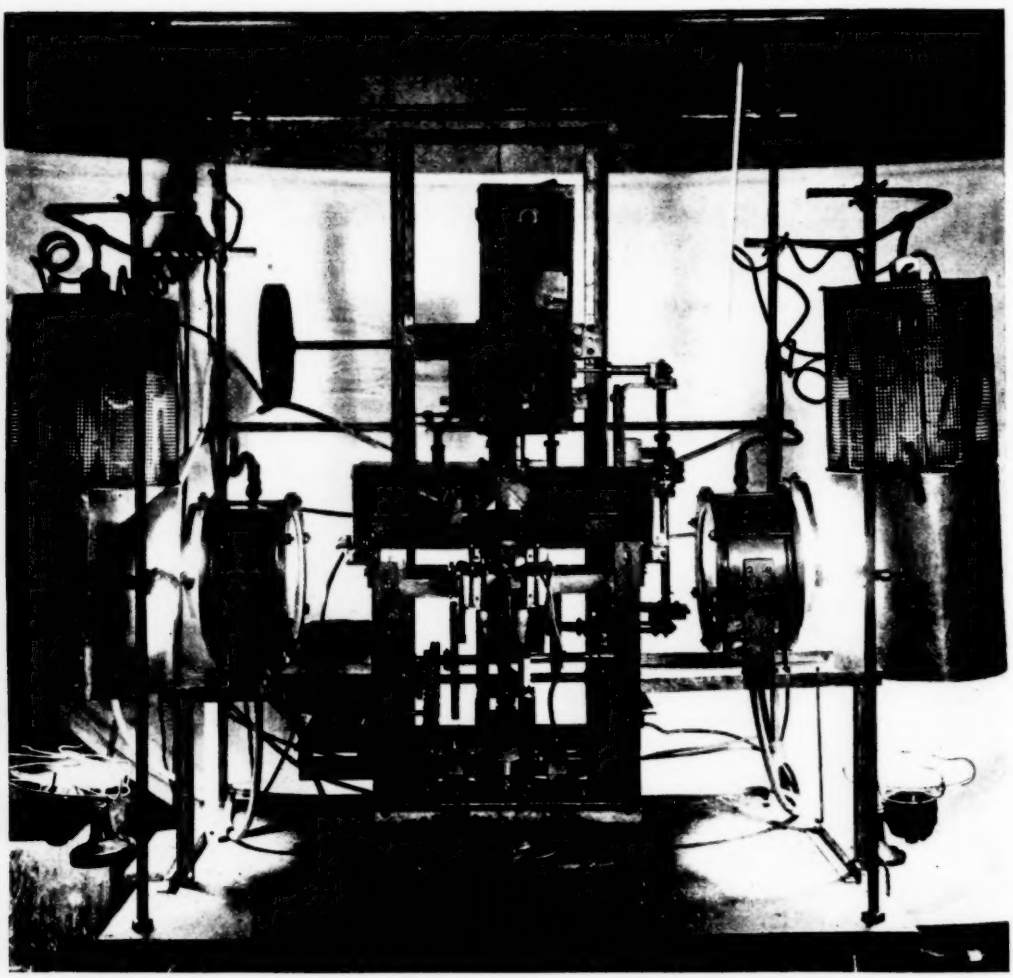

Fig. 1. Modified Shimizu-Wilson apparatus.

Experiments on the Synthesis of Oxygen Atoms of Mass 17

The Wilson Cloud-track apparatus used in this laboratory since 1923 was again modified, Fig. 1, and 39,000 photographs, each with two views

[3] Pettersson-Kirsch, Atomzertrümmerung, p. 139–40.

at right angles, were taken. The gas used was nitrogen, and the α-rays were obtained from thorium C and C′ as before.

Since the photographs represented about 10 tracks per picture, the number of α-rays used in this work was 390,000, and of these about 250,000 were of long range (8.3 cm) from thorium C′.

From these experiments two disintegrative-syntheses of oxygen 17 were obtained, and one view of one of these is shown in Fig. 2. The remaining range of the α-particle is 6 cm, its velocity 1.86×10^9 cm, and the velocities of the proton and of oxygen 17 are about 3×10^9 cm and 0.31×10^9 cm per second, respectively.

Results and Discussion

In each of three sets of experiments a quarter of a million α-rays of long range were shot through nitrogen. The yield per million fast α-rays of disintegrative syntheses represented by the following equation

$$N^{14}{}_{7+}+He^{4}{}_{2+}\rightarrow O^{17}{}_{8+}+H_{1+}{}^{1.0073}$$

was 8, 29, and 8, respectively for the work of Harkins and Shadduck, of Blackett,[4] and of the writers.

These results are of somewhat more interest if compared with the number of elastic collisions in which no disintegrative syntheses were involved (Table I).

Table I. *Number of disintegrative syntheses as related to the number of elastic collisions in which the α-particle was deflected through more than 90° (per million α-rays of 8.6 cm range).*

	Elastic collisions	Non-elastic collisions or disintegrative syntheses	Sum
Harkins and Shadduck	22	8	30
Blackett	32	29	61
Harkins and Schuh	100	8	108
	154	45	199

The number of inelastic collisions is about 29 percent as large as the number of collisions in which the α-particle is deflected by an angle greater than 90°. It is apparent, however, that the number of events of either type is too small to give an accurate knowledge of the ratio. In the observations recorded in this laboratory, only about 4 cm of the 8.6 cm range of the fast rays was photographed, but this was the effective region of highest velocity.

Since only about one atom of nitrogen in 800 has an atomic weight of 15 (isotopic number = 1) it is evident, since approximately a fourth of the total number of sharp collisions result in disintegrative syntheses, that the nitrogen affected is in general that of atomic weight 14 and isotopic number 0, which constitutes almost the whole of atmospheric nitrogen.

It seems probable that at least a part of the atoms of mass 17 in atmospheric oxygen are formed by this particular disintegrative synthesis. There is also in the atmosphere a still more abundant oxygen isotope of mass 18

[4] P. M. S. Blackett, Proc. Roy. Soc. **A107,** 349 (1925).

and isotopic number 2, which, if formed by an entirely similar process, could only come from the less abundant nitrogen isotope of mass 15.

In this connection it may be noted that while the higher isotopes (17 and 18) of oxygen are very rare in comparison with the 16 isotope, nevertheless, *provided the oxygen of rocks has the same composition as atmospheric oxygen*, these seemingly rare isotopes are actually about as abundant on earth as ordinary nitrogen.

In connection with the problem of the origin of the higher isotopes of oxygen, it would be important to obtain and analyze the band spectrum of oxygen from non-radioactive minerals, and particularly from oxygen compounds present in meteorites. Unfortunately it is difficult to determine the

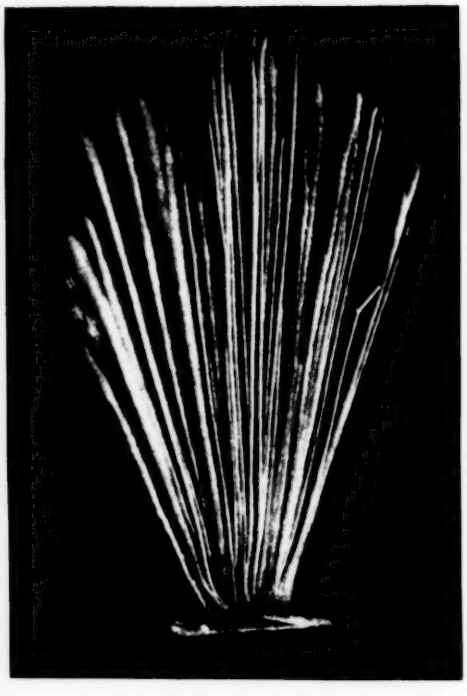

Fig. 2. Disintegrative synthesis of oxygen 17 and hydrogen from nitrogen and helium.

minute amount of the isotope 17 in experiments in the laboratory, since at ordinary pressures the intensity of the absorption band is too small, and the use of high pressures causes a considerable error due to a change in width of the lines and a resultant effect upon the apparent intensity.

Table II gives the abundance of the different atomic species of the elements nitrogen and oxygen as nearly as is now known.

If the oxygen of the earth's crust has the composition of that in the atmosphere, the isotope of mass 17 cannot have been formed entirely by the disintegrative synthesis from nitrogen in any reasonable period unless the amount of radioactive material was formerly very much greater than at present. For example, provided the effective α-rays passed through ni-

TABLE II. *Abundance relations for nitrogen and oxygen and carbon in the twenty-mile crust of the earth (atomic percentage).*

At. No.	Element	Atomic weight	Isotopic	Atomic percentage
8	Oxygen	16	0	57.38
6	Carbon	12 and 13	0 and 1	0.152
8	Oxygen	18	2	0.057
7	Nitrogen	14	0	0.022
8	Oxygen	17	1	0.007
7	Nitrogen	15	1	0.000027

trogen alone, it would require a period of the order of 10^{14} years for the known radioactive material to give the requisite amount of oxygen 17. Since, however, only about one atom in 4,000 in the crust is nitrogen, the period required would be of the order of 10^{18} years, since the stopping power of nitrogen is less than that of the average atom. It would take an extremely large error in the estimated amount of radioactive material in the earth's crust, and in the yield of oxygen 17 from nitrogen, to reduce this period to 10^{16} years, which is very much in excess of the supposed life of the earth. The simplest assumption is that oxygen 17 has been formed by other processes, although there is no need to restrict the time for the formation of this species from nitrogen to the period of existence of the crust of the earth. If oxygen 17 should prove to be very much more abundant in the oxygen of the atmosphere than in that in rocks, then it would be more probable that a considerable fraction has been formed by the disintegrative-synthesis.

The relations of the isotopes of oxygen to the other atomic species, and the relative abundance as well, indicate that the isotope of mass 16 and isotopic number 0 is by far the most stable, while that of mass 17 and isotopic number 1, is by far the most unstable. By analogy the nuclear spin of the zero isotope should be zero, and if recent estimates of the spins for the cadmium isotopes are correct, it seems probable that the spin (in units $h/2\pi$) is also zero for isotope 2, and equal to 1/2 for the species of isotopic number 1. Thus it seems probable that the oxygen isotope of mass 17 produced by bombardment of a nitrogen nucleus by an alpha-particle, should exhibit a hyperfine structure in its line spectrum, and an alternation of intensities in its band spectrum (alternate lines not missing).

If the nitrogen molecule has a radius of 1.47×10^{-8} then in order to obtain one non-elastic collision, that is one disintegrative synthesis, a fast α-particle would need to shoot through 3.2 billion; to obtain an elastic collision, through five hundred million; and for any collision, through 370 million nitrogen molecules. In each molecule there are two nuclei which may be hit. On this basis the diameter of the nitrogen nucleus is of the order of 10^{-12} cm. This is of the general order of size found by Geiger and Marsden ($3.\ 2\times10^{-12}$ cm.) for the nucleus of an atom of gold.

The number of deflections of the α-particle through more than 90 degrees is very large in comparison with the deflection through smaller angles, and in agreement with other work this indicates that the inverse square law does not hold at the small distances of approach between the α-particle and the nucleus of the nitrogen atom.

SOME INVESTIGATIONS INTO THE VELOCITY OF SOUND AT ULTRA-SONIC FREQUENCIES USING QUARTZ OSCILLATORS

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(Received February 10, 1930)

Abstract

The velocity of sound at ultra-sonic frequencies is measured over a frequency range from 40 to 216 kilocycles per second using quartz crystals as sound oscillators. The emitted sound is reflected back upon the source and as its phase changes the plate current of the quartz oscillator goes through a series of maximum values. The distance moved by the sound reflector between these maxima is a half wave-length of the emitted sound.

The velocity is obtained in air free from CO_2 at three values of the relative humidity, dry, 45 percent relative humidity at 20°C, and in air saturated with water vapor at 20°C.

The velocity is found to change with the distance from the source, becoming smaller as the distance becomes greater. This was particularly noticeable at 42 kilocycles.

At a distance of 45 centimeters, all values except those below 60 kilocycles become within 0.03 percent of an asymptotic value of 331.60 meters per second.

The velocity is found to depend upon the number of wave-lengths from the source.

The effect of humidity upon the velocity is found to be expressed by

$$V_H = V_0 + 0.14H$$

where V_0 is the velocity in dry air at 20°C and V_H is the velocity at any relative humidity "H" at 20°C.

THE scope of the present work was intended to include the measurement of sound velocities from about a frequency of 40 kc up to 2000 kc in several ordinary gases. Actually the investigation up to the present has been limited to measurements in air for other problems came by the way which needed solution before the research could be pushed further. As a start it was decided to check the work which had been done in air by Professor Pierce,[1] in particular, to see if the considerable increase in velocity reported by Professor Pierce for the region about 40 kc could be checked. This turned out to be somewhat difficult, and the problem has become a study of the velocity in air in the frequency range from 40 to 216 kilocycles and at various distances from the source. The effect of humidity upon velocity has been studied experimentally. The results seem to shed some light upon the reported increase in sound velocity at 40 kilocycles and indicated that the whole phenomenon is extremely complicated and interesting.

In the following experiments, the control and measurement of four variables constituted the major part of the problem in hand. These were, the

[1] G. W. Pierce, Proc. Am. Acad. of Arts and Sciences **60**, No. 5 (1925).

wave-length of the emitted sound; the frequency of this sound; the temperature at which the measurements were made; and finally, the constitution of the medium through which the waves were propagated.

As in Professor Pierce's paper the sound was produced by means of quartz crystals, the use of which has by this time become quite common as frequency-control devices. If quartz crystals are used in conjunction with a vacuum tube circuit of the proper sort, the circuit will oscillate electrically with a frequency determined by one of the natural mechanical periods of vibration of the crystal. Such a circuit based on Figs. 5 and 6 of Professor Pierce's paper is shown in the accompanying diagram, Fig. 1, together with an amplifier.

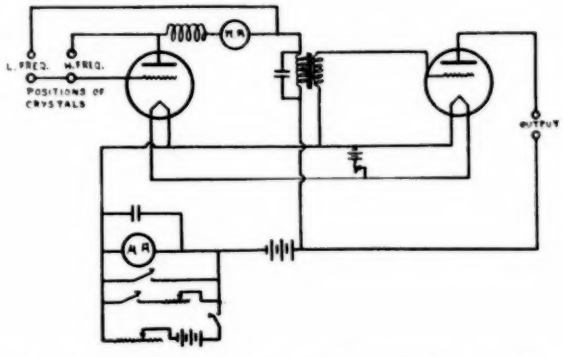

Fig. 1. The oscillating circuit together with the audiofrequency amplifier and microammeter, showing shunting and bucking arrangement for the microammeter.

The Measurement of Wave-length

Simultaneously the mechanical motion of the crystal produces longitudinal elastic waves of the same frequency in the medium in which it is situated. To measure the wave-length of such a disturbance a very convenient method is available. It has been found by Professor Pierce that if a solid reflector be moved in a direction perpendicular to the sound emitting face of the crystal so that the sound is reflected back to the crystal face, small changes occur in the plate current of the circuit shown. This current goes through a series of maximum and mimimum values as the reflector is moved. The distance between successive maximum values of the current represents a half wave-length of the emitted sound. Since this change is small in comparison with the steady plate current, it may be detected more readily by means of a microammeter which is made to read zero for the normal plate current by means of a local bucking battery and a proper variable resistance. It was also convenient to have a variable shunt and short-circuiting switch, as indicated in the diagram, Fig. 1. Such an arrangement made it possible to use current variations of as little as four microamperes to determine the wave-length.

The position of the reflector was obtained by means of a precision screw of half millimeter pitch provided with a micrometer head divided into 100

parts so that one division on the dial indicates a motion of 0.005 millimeters. This screw was calibrated under actual working conditions by checking against a good standard meter for every five centimeters of length.

The Measurement and Control of Frequency

The frequency of the sound source was measured in terms of a standard crystal which was kept in a fixed position during any set of measurements. This standard was calibrated directly from the clock at the Harvard Observatory by means of the method of coincidences described by Professor Pierce.[2] Its frequency was known at any one temperature and its temperature correction was also known. The value of this frequency was close to 421 kilocycles. At any temperature its frequency was known to about three parts in four hundred thousand.

All the crystals used in this experiment had been cut by Professor Pierce and had been ground by him so that they had a frequency such that some harmonic would produce an audible beat with the 421 kc standard. The frequency of this audible beat with the standard was measured on a calibrated

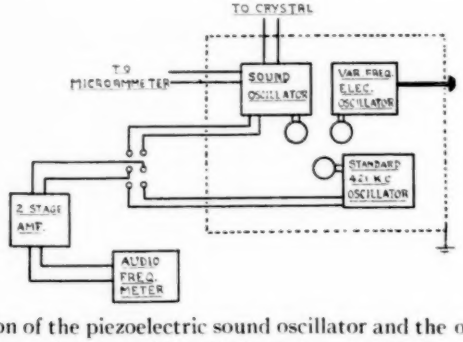

Fig. 2. Relative position of the piezoelectric sound oscillator and the oscillators and amplifiers used in determining the frequency of the sound.

audiofrequency meter and could be determined within two or three cyles per second giving an accuracy better than one part in one hundred thousand in the frequency of the sound source. The harmonic was identified by means of a wave meter.

The control of the frequency offered no difficulty, as the crystals once oscillating continued at constant frequency so long as they were undisturbed. The frequency measured at the beginning and at the end of each run was never significantly different. The disposition of the oscillators is shown in Fig. 2.

The Measurement and Control of Temperature

The effect of temperature on velocity was computed from the known relation between velocity and temperature. If one wishes an accuracy of 0.01 percent or better, then the temperature must be measured within 0.05°C.

The temperature was measured by means of a mercury in glass thermometer (No. 6466) divided directly into tenths of degrees centigrade which

[2] G. W. Pierce, Proc. Am. Acad. of Arts and Sciences **63,** No. 1 (1928).

could be read to 0.02°C. This was placed within 10 centimeters of the vibrating air column. Precaution was taken to have it at the same vertical height as the crystal, so that any vertical temperature gradient would be avoided.

This thermometer was compared with a German Standard thermometer (P.T.R. 42547) kept in the Jefferson Coolidge Chemical Laboratory. The thermometer was carefully calibrated against this throughout the range over which it was used. This range was only five degrees in length, viz. 18.00°C. to 23.00°C. Corrections have been applied as they were found in the calibration.

The problem of keeping the air at nearly constant temperature forced the apparatus to be arranged in a manner such that the sound chamber was in a separate room from the operator. This room was only entered when crystals were changed, and its temperature altered very little since the room was below ground level and had no windows and no heating system. During the period over which a single set of measurements were taken, say half an hour, the observed reading on the thermometer seldom changed perceptibly. This thermometer was read from the operator's room by means of a short focus telescope. Since the room was undisturbed and the sound container was metal, it was believed that this observed value indicated accurately the temperature of the enclosed air. This is further substantiated by the fact that on several occasions when air inside was thoroughly stirred, no variation of the reading took place, nor did any occur when the thermometer was forced more deeply into the container.

The Measurement and Control of Humidity

Professor Pierce had been lead to the conclusion that change in humidity produced little effect upon the velocity of sound at these frequencies, but since this is not true at lower frequencies, it was thought advisable to control this factor if possible.

The method used for the determination of humidity was that suggested in International Critical Tables[3] depending upon the constancy of the vapor pressure over saturated solutions of various salts. For example, if excess KNO_2 be dissolved in distilled water, the vapor pressure is such that the relative humidity at 20°C is 45 percent. Such a solution was placed inside the sound box while measurements were taken. A hair hygrometer placed in the sound box observed through a window served as an indicator for change in humidity.

When dry air was required the air was pumped through $CaCl_2$ and then over fused sodium hydroxide which also removed CO_2. To conserve drying agents and facilitate the drying, the intake of the blower was connected to the sound chamber and thus the same air was passed many times over the drying reagents. Beside this a dish containing P_2O_5 was placed in the container. When air saturated with water vapor was needed, a bubbler was put in series with the pump, and an open dish of distilled water replaced the P_2O_5. The CO_2 was removed by bubbling the air through a solution of NaOH.

[3] International Critical Tables Vol. 1, p. 67

Attention may be called here to the fact that while all results have been reduced to values at 0°C, the amount of moisture present is still referred to 20°C.

Alignment of Crystal

In most of the work the crystal was mounted on a platform rigidly attached to the gas container and was made level when the apparatus was in position. Later, a means of tipping the crystal was devised. It was found that the error produced by lack of alignment was small, for when the crystal was deliberately tipped, the change in length of a given number of half-waves was less than would have been predicted by the use of the cosine of the angle. The crystal was set by tipping it up and down until a maximum reaction was obtained with the reflector at a great distance away. In this manner the crystal could be lined within half a degree.

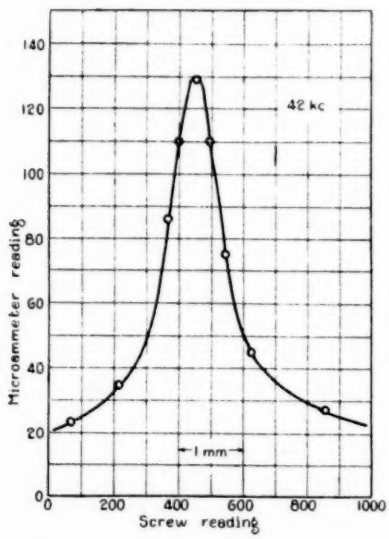

Fig. 3. A typical current peak a short distance from the source at 42 kilocycles per second.

Experimental Method for Location of Nodal Positions

While it was possible to measure frequency, temperature, and humidity quite as indicated in the preceding pages, the measurment of the wavelength was a question which turned out to be much more difficult in several respects.

If the readings of the microammeter be plotted against the distance as read by the screw, a series of maxima appear. These maxima will be referred to as "peaks" and the length of a half wave as the distance between two successive peaks.

To obtain the position of the peak with the greatest accuracy, it was impossible to set on it by moving the reflector to the position where the meter gave its largest reading, for it was found that in all cases the top of the peak was flat over a number of scale divisions. This is evident from Fig. 3. To

avoid this, readings on either side of the peak were taken (e.g. when the meter reads "110"). At this point the motion of the needle was great for a small displacement of the piston. Thus the reading can be made with greater accuracy. The mean position of the reflector on the two sides of the peak was taken as its true position.

Back lash existed, but its effect was avoided by taking readings travelling first in one direction and then in the opposite. This also avoided trouble due to change in back lash from point to point. The calibration of the precision screw was also carried out in this manner. Even without any back lash the position of the peak in space is different when the reflector is being moved out from that when the movement of the reflector is in the opposite direction.

Hence a mean position of the reflector going in and out has been taken in every case. The procedure is illustrated by the following readings taken to determine the position of the maximum.

1. Reflector moving in
   57707 meter reading increasing
   57665 meter reading decreasing
   57686 average
2. Reflector moving out
   57732 meter reading increasing
   57764 meter reading decreasing
   57748 average
3. Actual position
   57686
   57748
   57717 average
4. Difference between two indicated positions
   57748
   57686
   62 divisions
5. Known back lash 48 divisions
6. Shift of position independent of back lash is 14 divisions.

The shift in "6" is not constant, but by using the above method the length of an interval could be determined consistently, with an accuracy dependent upon the frequency of the sound emitter, but seldom with an error of more than ± 3 divisions on the graduated wheel and usually not more than ± 1.

Possible Percentage Error

Having dealt with the control and measurement of the four variables concerned, it is interesting to note the accuracy with which sound velocities might be obtained under such conditions. Let us suppose 50 centimeters of the screw could be utilised for measuring purposes and that the maximum points could be located to two divisions on the wheel. The percentage error thus introduced would be 0.004 percent. The frequency can be found to better than one part in thirty thousand and hence introduces a possible error less than 0.003 percent. The temperature can be measured to 0.02°C and thus introduces an error of four parts in one hundred thousand or 0.004 percent. Since the air is kept at a fixed humidity the accumulated percentage error may amount to as much as 0.01 percent.

The work had not progressed very far before it was observed that the number of variables concerned had been underestimated, for with all possible precautions results did not check each other unless taken at exactly the same distance from the vibrating crystal.

Precautionary Experiments to Prove Reality of Change in Wave-length

It must be noted here, that the word "velocity" is used to denote the product of the measured frequency and distance moved by the reflector between alternate "peaks" of current in the plate current of the oscillator. The words "half wave-length" will be used to denote the distance moved by the reflector between peaks.

It was found that velocities computed from measured intervals close to the crystal showed a marked increase in magnitude. While this seems to be true to some extent at all frequencies, the effect is much more marked in the case of 40 kc and most of the experimenting has been done using this frequency.

In order to give an account of these experiments, it will be necessary to describe briefly the apparatus in use at this time. This consisted of a brass box containing two compartments connected by a rectangular opening. In one of these compartments the crystals were arranged on a movable slide in such a way that any crystal which was to be used could be moved to a position where it could radiate sound into the adjoining chamber. This has been designated "the sound chamber." The whole box was mounted on one end of a lathe bed which supported the measuring screw. As a result only a little more than half of the total length could be used for measuring. The reflector was on the end of a piece of one-inch brass tubing which passed through a snug-fitting gland in the end of the sound chamber remote from the crystal. This made a system that was tight enough to prevent very much diffusion of gas from the outside.

The aperture which led from the crystal chamber was larger than the largest crystal face, and hence all radiation from the face entered the sound chamber. The latter had a square cross section 18 centimeters to a side and had a length of about 35 centimeters. The actual interior space was really smaller than this due to the padding.

Padding was always necessary, but no change in it altered the fact that high results were obtained close to the crystal face. The size of the reflector was altered with no results. A felt tunnel was constructed of the same size as the reflector, but this produced no change. A felt pad of cross section equal to that of the sound chamber was fastened to the back of the reflector, and hence the length of the box changed with each setting. Thus any resonant effect due to the fixed size of the sound chamber should be discovered. This also failed to produce any decrease in the wave-length. Two crystals having approximately the same frequency but with different areas of radiating faces were available, both of which produced similar high results.

It was thought that the sagging of the reflector due to its own weight might introduce errors. This would be specially true when the reflection was near the crystal face at which time it hung far out from its support. With this in mind, one of the crystals was set up outside the chamber and the length of groups of waves measured in a region quite close to its face. Then the crystal was moved closer to the lathe bed and the readings repeated. The same in-

crease was noted, but this time the piston hung only half the distance over its support. Thus it was decided that there was no measureable error due to the sagging of the reflector.

At the same time the effect of placing objects in the vicinity of the vibrating column was tried. It was found that even when solid objects were placed but a few centimeters below the direct path of the sound, no noticeable change was made in the position of a particular peak which had been located previously.

Rough measurements made at this time indicated that for all the frequencies used an increase in wave-length could be noted close to the source with or without the container.

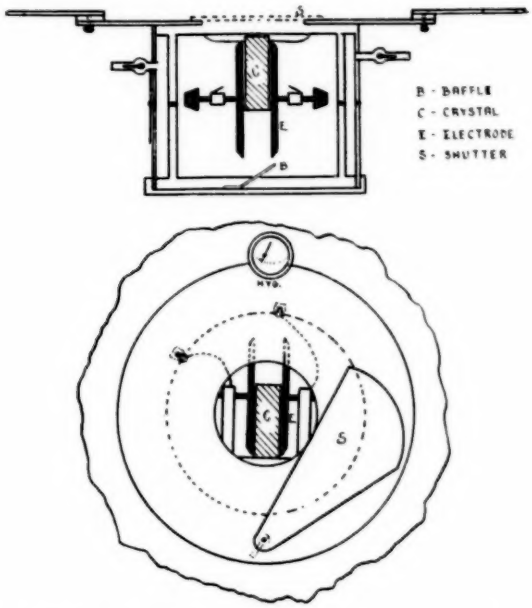

Fig. 4. Two views of the crystal holder and crystal chamber. a. Horizontal section of crystal and holder. b. Elevation of crystal and electrodes as viewed from within sound chamber.

Description of Apparatus

As a result of these experiments, it was concluded that the inequalities of the distances between peaks were real and that sound velocity determinations carried out in this way gave values apparently different for different distances from the source and suggested measurements at greater distances from the source. This made it necessary to reconstruct the chamber of the apparatus. The revised disposition of this apparatus has been partly described in the general discussion, but since the revised arrangement has been used for all measurements recorded here, a fuller description is warranted. The revised arrangement consisted of a sound box long enough to permit the use of the full length of the measuring screw, and of sufficient diameter to permit its use without padding the walls. The actual dimensions were 60 centimeters

in length and 45 centimeters in diameter. The crystal holder had circular electrodes whose distance apart could be changed easily. The crystal con-

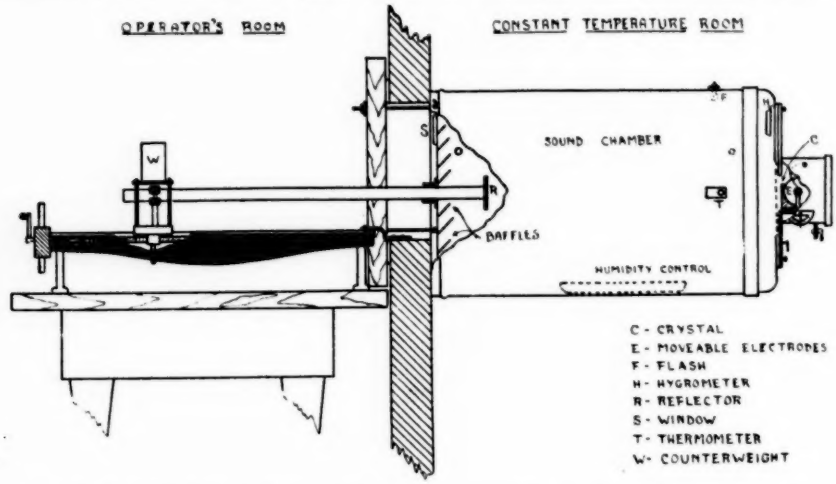

Fig. 5. A general view of the position of the precision screw and sound chamber.

tainer was arranged to permit easy access without opening up the whole sound chamber to the outside air. This was attained by having a slide that could be used to cover the aperture between the crystal chamber and sound box when crystals were to be changed. This slide is shown in the diagram, Fig. 4 by a dotted line. Since the whole container was located in a separate room, the temperature stayed very constant as mentioned.

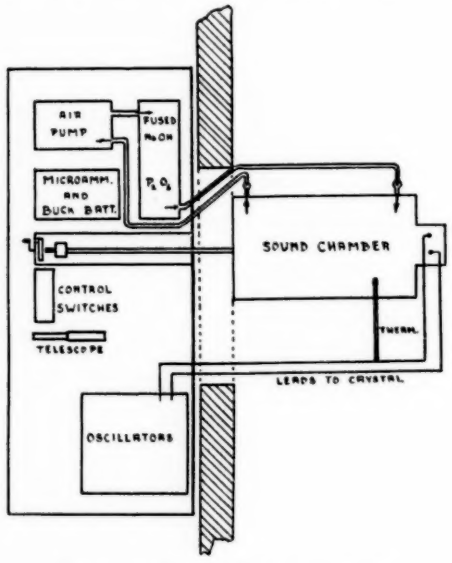

Fig. 6. A plan of all the apparatus.

An attempt was made to shield the lead which went from the piezo-oscillator circuit to the crystal, but the crystals refused to oscillate. The

leads were kept apart for best results. A complete diagram of the apparatus is appended in Fig. 5 and the disposition of the apparatus is shown in Fig. 6.

Experimental Method

The procedure for taking data was as follows. The sound oscillator was started, and the switch putting the bucking battery in circuit was closed. This was allowed to run for at least half an hour so that the change in voltage of the bucking battery would not cause the needle of the microammeter to drift. Immediately before the reflector was moved, the temperature of the air was taken, and the beat note with the standard crystal was recorded. Then the position of peaks for equal intervals of from 10 to 50 half waves were recorded as rapidly as could be done conveniently. This completed, the temperature and frequency were taken again, and averaged with the values taken before the run.

Method of Using Data

The fact that the wave-length changes with position makes it necessary to alter the method of averaging employed previously. The method used by

Table I.

Freq. (kc/sec.)	Veloc. (m/sec.)	No. of runs	Distance from source (cm)	Distance from source wave-lengths
42	333.24	8	12	15
42	332.14	4	20	25
42	332.12	8	32	40
42	332.07	7	40	50
42	331.75	6	53	65
60	332.17	4	12	20
60	331.94	15	29	50
60	331.82	17	40	70
60	331.73	17	52	90
70	332.34	3	12	24
70	331.63	8	30	60
70	331.92	8	40	80
70	331.63	8	51	105
84	331.94	2	20	50
84	331.63	11	29	75
84	331.76	6	35	85
84	331.72	11	51	125
84	331.77	6	51	125
105	331.79	7	17	53
105	331.62	7	32	100
105	331.73	11	40	125
105	331.61	8	49	150
105	331.65	12	49	150
140	331.82	3	16	65
140	331.67	7	32	130
140	331.75	4	32	130
140	331.63	9	32	130
140	331.60	7	49	200
140	331.67	4	49	200
140	331.60	9	49	200

Professor Pierce[1] assumes the presence of equal intervals, the only difference being the experimental uncertainty of measurements. In the present case this is not true except in a limited region for the two highest frequencies used.

The manner in which the results were finally computed was decided after most of the runs were made. The readings were taken as if Professor Pierce's method were to be followed, but the method actually used is described below.

The average wave-length was taken over a distance which could be measured with an accuracy of better than 0.01 percent (viz., three hundred turns of the screw, or 15 cm). *This gave the mean velocity about a point midway between the ends of this interval.* The number of half wave-lengths used was dictated by convenience so long as the total interval did not greatly exceed three hundred turns of the screw. The average was found merely by taking the difference between the end points and dividing by the number of wave-lengths in the interval. When the waves were equal in length in the interval, the average obtained in this way did not differ significantly from that obtained by Professor Pierce's more elaborate method.

The results have been calculated for the most remote 15 centimeters of the screw, then for the next 15 centimeters, and so forth. The distance from the crystal face in wave-lengths at which the results may be considered as average velocities has been listed in Table I. In most cases the 15 centimeter divisions are only approximate as will be seen upon referring to the table.

The results tabulated in Table II are those computed from readings taken over a distance about 15 centimeters in length at an average distance of 45 centimeters from the source.

TABLE II. *Dry air at 0°C. free from CO_2.*

Freq. (kc/sec.)	No. of runs	Velocity m/sec.	Freq. (kc/sec.)	No. of runs	Velocity m/sec.)
140	16	331.60	70	8	331.63
105	20	331.63	60	17	331.73
84	17	331.74	42	6	331.75

If this velocity be assumed constant, the maximum variation from the mean is 0.08 meters which is 0.024 percent and is within the limit of error of the experiment.

Taking the average velocity over the same region, remote from the source I have found the following (Table III) for air free from CO_2 at 45 percent humidity at 20°C.

TABLE III. *Air, free from CO_2 at 45 percent relative humidity at 20°C.*

Freq. (kc/sec.)	No. of runs	Velocity m/sec.	Freq. (kc/sec.)	No. of runs	Velocity m/sec.
140	8	332.20	70	8	332.31
105	7	332.27	60	10	332.16
84	8	332.28	42	5	332.38

With the same conditions as above, we have a maximum deviation from the mean of 0.06 meters which is 0.018 percent, which is also within experimental error.

The values of the velocity in air saturated with moisture are not so consistent due to the fact that the crystals would only oscillate for a few minutes in the moist air and measurements were necessarily hurried. This was more serious at low frequencies where more time was needed to make the measurements. Results are given here (Table IV) for four different frequencies. These results were found for the sections of the sound chamber most remote from the crystal.

TABLE IV. *Water saturated air, free from CO_2 at 20°C.*

Freq. (kc/sec.)	No. of runs	Velocity m/sec.	Freq. (kc/sec.)	No. of runs	Velocity m/sec.
140	14	332.97	84	6	332.86
105	8	333.00	42	4	333.34

The maximum variation here is 0.16 meters which gives 0.05 percent, which is a little worse than the other results. The results in Tables II, III, and IV are plotted in Fig. 7.

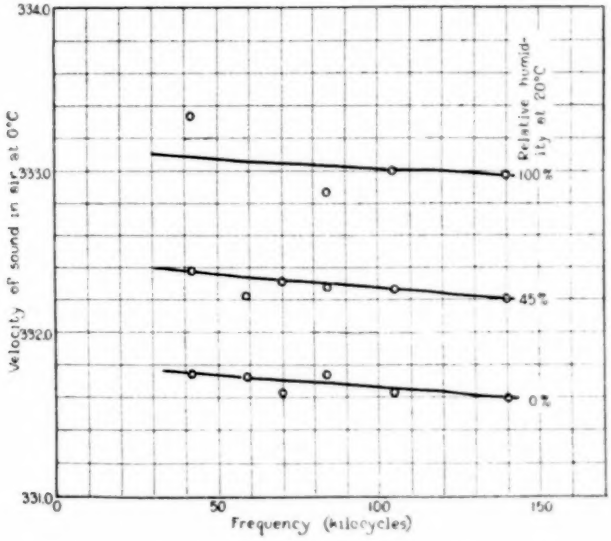

Fig. 7. The velocity of sound in air at 0°C at different frequencies and under different humidity conditions.

By taking the average values at all frequencies for dry, 45 percent humidity, and saturated air we obtain the following velocities in meters per sec.

Dry	45% relative humidity	Wet
331.68	332.27	333.05

These values of the velocity are plotted against the relative humidity at 20°C in Fig. 8. For convenience the actual values of velocity have been reduced to 0°C.

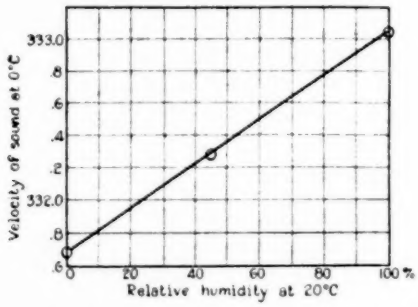

Fig. 8. The relation between the average values of the velocity of sound at all frequencies and the relative humidity at 20°C.

As a result the velocity "V_H" at any relative humidity at 20°C, is related to the velocity "V_0" in dry air at 20°C by the equation.

$$V_H = V_0 + 0.14H$$

where "H" gives the value of the relative humidity (i.e., that fraction of the amount of moisture which would be required to saturate the air at 20°C).

In addition to the values for the velocity in dry air given in Table II, some further values have been obtained using a so-called direct current amplifier which has been built in order to work at points still more remote from the crystal.

The values tabulated below are the average values taken in a region beyond 40 centimeters from the face.

TABLE V.

Freq. kc/sec.	Velocity at 0°C meters/sec.	Freq. kc/sec.	Velocity at 0°C meters/sec.
216	331.66	70	331.56
140	331.64	60	331.63
105	331.61	54	331.87
84	331.61	42	332.00

As in the preceding work, the values for the low frequencies seem high.

VARIATION OF VELOCITY WITH DISTANCE FROM FACE OF CRYSTAL

The fact still remains that the values of this velocity seem to vary with distance from the crystal, and enough data are available to give some idea of how this variation takes place. In Fig. 9 the values of the velocity are plotted against frequency for intervals at different average distances from the source. In Fig. 10, the same values of the velocity are plotted against the average number of wave-lengths from the source, at which the measurements were made.

From the former plot, it will be seen that as the chosen interval becomes more remote from the source the values of the velocity approach more nearly

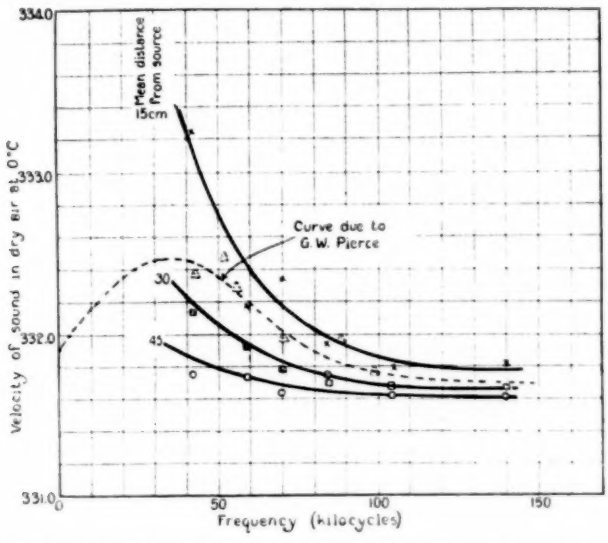

Fig. 9. The relation between the velocity of sound at 0°C and different frequencies to the distance from the sound source at which these measurements were taken.

a common value. The greatest deviations from this common value occur at the lower frequencies.

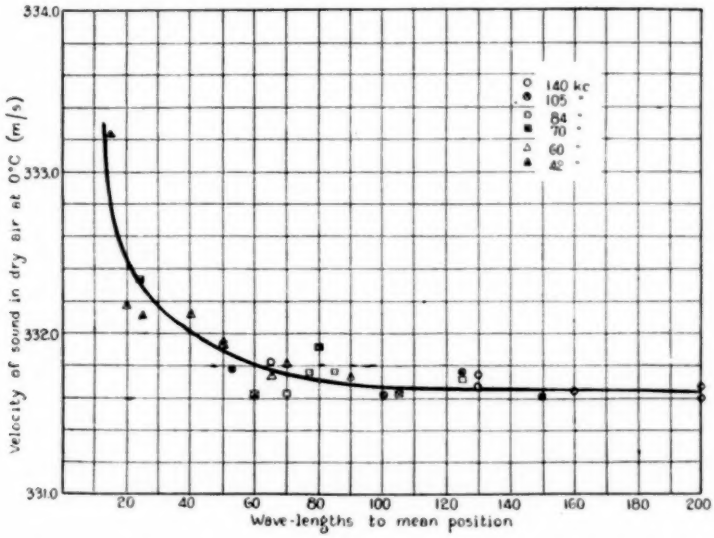

Fig. 10. A curve showing the relation between the velocity of sound, as measured by this method, with the number of wave-lengths from the source, for the frequencies indicated.

It will be seen from Fig. 10 that the size of this deviation depends upon the number of wave-lengths distant from the source at which the measurements are taken.

It will be noted that to obtain the velocity values shown in Fig. 10 it was necessary to make the readings over a considerable distance. For lower frequencies this meant about 40 half waves, while for the frequency of 140 kc this number is of the order of 150 half waves. Hence the closest permissible values at 140 kc will give a mean velocity about 75 wave-lengths away. It will be seen that an increase in velocity in the vicinity of the source would be

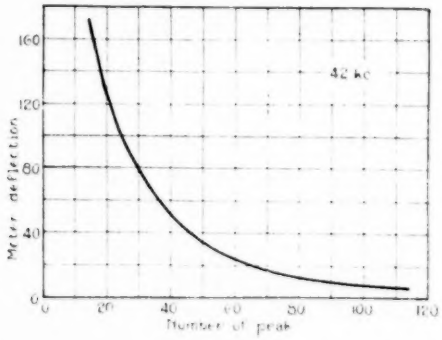

Fig. 11. A plot of the amplitude of 36 consecutive peaks (reading of microammeter against distance) against the number of the peak (starting from the source).

masked in this manner. Thus no real close-up values have been obtained for the higher frequencies. Similar experimental difficulty presents itself at a large number of wave-lengths for the lower frequencies, as the most extreme position at 42 kc was only 80 wave-lengths, and it seems improbable that this is far enough to give the asymptotic value obtained at a great distance.

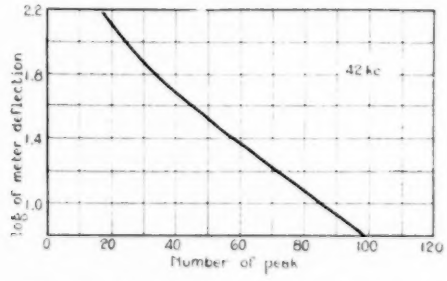

Fig. 12. The logarithm of the deflection plotted in Fig. 11.

Since the velocity close to the source could be studied better by means of the 42 kc crystal, some extra attention has been bestowed upon this. Starting from a position about fourteen half wave-lengths from the source, the next 36 consecutive peaks were plotted (ie., the reading of the microammeter was plotted against the distance), from this point on, every tenth wave was plotted until the 129th half wave was reached.

From these curves a decrement curve, Fig. 11, was plotted to a different scale and also the logarithm of the microammeter deflection, Fig. 12. The latter was very nearly a straight line except for the first few readings. The

decrement was found to be 0.015 per half wave. This is altogether too small to affect the velocity to the extent which is indicated by these experiments.

A graphical examination was made to ascertain the shift in the position of the peak due to this decrement and the effect of the decrement on the position of the peak was found to be negligible. Since the equation of the reaction current was unknown, this was the only available method.

It is worth noting that in addition to the change in wave-length with distance from the source, variations beyond experimental error occur in the separate intervals at the lower frequencies and in extreme cases amount to about 0.5 percent of the length of the interval when this is in the vicinity of the source.

Summary and Discussion of Results

An attempt has been made to obtain the value of the velocity of sound at frequencies from 40 kc to 216 kc under conditions simulating outdoors, but at the same time to have greater control over the variables concerned.

Values have been obtained at eight different frequencies for three humidity conditions and at different distances from the source. An apparent rise in wave-length has been noted for regions close to the source, but which at any given position is greater the lower the frequency. As one recedes from the face of the oscillator, the velocities at various frequencies appear to approach a common value. If the velocity as found for all frequencies be plotted against the mean distance from the source in wave-lengths, some relation appears. A study at 42 kc shows that as the reflector recedes from the crystal, the value of the microammeter deflection (the change in plate current in the oscillator) decreases smoothly with a decrement nearly logarithmic, but too small to affect the length of the interval appreciably.

The method employed here has the advantage over tube methods since there is no tube correction to be considered. With the apparatus used, the diameter was equal to sixty of the longest wave-lengths used. This would correspond to a room about 60 feet in diameter for sound of about 1000 cycles.

While it is quite probable that some trouble arose due to reflections from the walls, it is hoped that at some distance from the source such effects are small. Small variations were noted from day to day which may have been due to this cause. Small temperature changes would cause marked alterations in any disturbance of this sort, as the path of wave reflected from the sides of the sound chamber would be much longer than that of the direct beam.

The rise in velocity near the sound source has been observed before. At Chicago in 1905 T. C. Hebb,[4] working in a large hall with audible sound of wave-length approximately 10 inches, found this same effect. He noted the increase in the wave-length as the source was approached and specifically mentions that it was beyond experimental error. The length of the wave seemed to approach a limit as he reached positions fifty to sixty wave-lengths from the source. A shorter wave-length used seemed to make the trouble less obvious, though it was noted that he was farther from the source to begin

[4] T. C. Hebb, Phys. Rev. **20,** 89 (1905).

with and took a greater number of waves for his average length. No explanation was offered save that he thought that his reflecting mirrors were not large enough for the first wave-length he used. Since the above experiment was similar to the present experiment in many ways, it is interesting to note a similar phenomenon was observed.

The cause of this rise in velocity near the source has not been determined definitely so far, but several possibilities present themselves. Regnault found that velocities near the source were high and assumed that this was due to intensity. This can scarcely be true here as the energy radiated as sound is extremely small, for the input to the crystal oscillator, (exclusive of filament) was less than one-tenth of a watt. Some apparent increase would result from the lack of a plane wave system when a comparatively large reflector is used. However the effect is too large to be altogether accounted for by this argument.

An investigation using two crystals with different faces but having the same frequency indicated that the face of the crystal affects the result when the reflector is close to the face. Furthermore it seems probable from some recent work that in the case of higher frequencies no large rise in velocity takes place. A recent experiment showed that this was true when a 54 kc crystal with a small face was used. It is difficult to study the effect of the shape of the crystal face as they are not available in general with differing faces and the same frequency.

It is difficult to see why the reaction in the microammeter should fall off smoothly when passing through a region which must have an elaborate diffraction pattern, unless the reflector was large enough to average out diffraction effects.

The values of the ratio of the specific heats of air deduced from the velocity at 140 kc which seems to be close to the asymptotic velocity, Fig. 10, is 1.4035. This is in good agreement with the average of the best results today, computed from the velocity of sound at audible frequencies.

The average velocity in dry, CO_2 free, air as computed from the values at six frequencies is 331.68 meters per second. This result is felt to be too high, and if measurements at greater distances from the source could be taken for the lower frequencies, it seems that the results ought to decrease to 331.60 meters per second, as this seems to be the asymptotic value.

It will be noted that if the investigator had been limited to any particular region on the screw the results would have indicated, Fig. 9, a higher value for the velocity especially at the lower frequencies. As the interval over which measurements were taken was moved further from the source this increase in velocity becomes less noticeable. A further examination of the data published by G. W. Pierce[1] was undertaken by Professor Pierce and the author and revealed that these measurements were taken in a region extending from the face of the crystal, out to a point about twenty centimeters distant. This will account for the similarity of the shape of the dotted curve, Fig. 9, with those obtained by the writer. Although the numerical values of the velocity are altered by the fact that no correction was made for humidity,

yet the humidity did not change appreciably during the experiments and hence the values lie along a curve similar to those obtained by the present investigator. Notice must be taken that no experimental values have been made below 40 kilocycles per second by this method, either by Professor Pierce or by the writer. The dotted curve, Fig. 9, is merely a reproduction of that published earlier.

The change in the velocity of sound caused by saturation with water vapor at 20°C has been found to be 1.37 meters per second. This agrees very well with values calculated by McAdie[5] and with values computed by the writer, assuming that the change in velocity is due to change in density only. Some work on this subject at audio frequencies has been done by Barss and Bastille,[6] but their results gave a change of only 0.57 meters per second.

An examination of Professor Pierce's note-book by Mr. W. J. Cahill has resulted in showing that at that time there was evidence of a change in velocity with humidity which was overlooked. This has been affirmed by Professor Pierce.

It may be added here that this work was done in three parts several months having elapsed between each set, and that the results check well. In one of these intervals the mounting of the standard was changed and recalibrated.

The following conclusions have been reached. The increase in apparent velocity at frequencies around 40 kc grows smaller as the measurements are taken in regions more remote from the source, and, the velocity in this range of frequencies does change with the humidity.

These experiments have been carried out in the Cruft Laboratory under the direction of Professor G. W. Pierce. Further experiments are now under way in this laboratory by the aid of which it is hoped that many of the present difficulties may be cleared up.

[5] McAdie, Annals of the Observatory of Harvard College **86,** 107 (1923).
[6] Barss and Bastille, Jour. of Math. and Phys. M.I.T. **2,** 210 (1923).

THE VELOCITY OF PROPAGATION OF LONGITUDINAL WAVES IN LIQUIDS AT AUDIO-FREQUENCIES

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Abstract

A method for measuring the velocity of propagation of longitudinal waves in liquids is described which is at the same time precise and convenient of application. A column of liquid contained in a cylindrical vertical steel tube was brought into resonance vibration at audio frequency by an electromagnetically excited diaphragm at the bottom. From the solution of the equation of propagation it is shown that when the resonance frequency of the system is the same as that of the diaphragm the reaction of the latter on the system is very small. The height of the column of liquid in the tube was adjusted until its natural frequency nearly corresponded with the predetermined resonance frequency of the diaphragm. The height was then varied slightly and the frequency adjusted until resonance occurred. From several observations of this type the appropriate height corresponding to the resonance frequency of the diaphragm was obtained by interpolation. The velocity of propagation of the longitudinal waves was then calculated from the relation $V=f_0\lambda$, where f_0 is the natural frequency of the diaphragm when clamped in the holder and λ is the wavelength.

Correction for the elasticity of the walls of the tube.—The correction formulas of Korteweg, Lamb and Gronwall were tested experimentally on tubes of different dimensions. The latter was found to give the most satisfactory agreement, the two former being unsuitable for precision measurements.

Measurements.—The velocity of sound was measured in air-free distilled water at 25°C. The average of 52 observations gave for this velocity 1485.4 ± 2.3 m/sec. From this value the bulk modulus, G, and the adiabatic compressibility, κ, were calculated. Curves were plotted illustrating the variation of the velocity of sound with temperature for the range 25°–70°C and with concentration for solutions of NaCl and KCl of different normalities. Curves for the corresponding variations of G and κ are also given.

A. Introduction

PRECISE determinations of the velocity of sound in liquids by resonance methods at audio-frequencies have not until recently been possible because of the uncertainty regarding the correction required to compensate for the elasticity of the walls of the tube. Wertheim in 1847 observed a large discrepancy between the velocity of sound measured by direct methods in large bodies of water and the velocity calculated from experiments with organ pipes filled with water from the same source. This difference was shown by Helmholtz[1] to be due to a lowering in the wave-velocity caused by yielding of the walls of the tube. Since then several correction formulas for this effect have been developed notably by Korteweg[2] and Lamb,[3] but the approxima-

[1] Helmholtz, Gesammelte Abhandlungen, Vol. **1**, p. 246.

[2] D. J. Korteweg, Wied. Ann. **5**, 525 (1878).

[3] H. Lamb, Memoirs and Proceedings of the Manchester Literary and Philosophical Society **42**, No. 9 (1898).

tions made are not sufficiently close to permit their use in precision measurements. A steel tube 4.32 cm in diameter and having a thickness of wall equal to 0.136 cm when filled with water requires a correction to the measured velocity of sound of 16 and 17 percent according to the Lamb and Korteweg formulas, respectively. Recently Gronwall[4] has derived a more precise correction formula. This has been tested by the writer under widely varying conditions in experiments described in the present paper.

Previous work on this problem has been done by Dorsing[5] and Busse.[6] The former from the measurements on the dust figures in a glass Kundt's tube has calculated the velocity of sound in several liquids with an estimated precision of about one percent; he made use, however, of the Korteweg correction formula. The latter using the same method with some slight improvements measured the velocity of sound in fifteen different liquids and by employing thick walled glass tubes reduced the magnitude of the Korteweg correction.

The purpose of the experiments described in the present paper was to develop a method for measuring the velocity of propagation of longitudinal waves in a liquid at audio-frequencies which would be at the same time precise and convenient of application. Preliminary experiments indicated that it was possible to produce resonance vibrations in a column of water contained in a vertical tube excited at the proper frequency by an electromagnetically driven diaphragm at the bottom, that the frequency which produced a maximum response for a given height of the column could readily be determined, and finally that the resonance curves were very sharp (for air-free water the sound intensity fell away to less than one half its maximum value when the frequency was changed by two or three cycles in the neighborhood of 1000~).

B. Apparatus

The original apparatus as it appeared when immersed in a thermostatically controlled oil bath is shown diagramatically in Fig. 1. The steel tube containing the liquid is shown at the left. Its dimensions were: length 101 cm, inside diameter 3.89 cm, outside diameter 6.37 cm. A chromium plated soft iron diaphragm 0.050 cm thick and the magnets from a Western Electric Co. 500 ohm telephone receiver were mounted at the lower end of the tube as shown in Fig. 2. The base consisted of a brass plate screwed over the end of the chamber containing the receiver; the tube itself stood on a horizontal plate fitted with leveling screws. To balance the static weight of the column of liquid and to prevent distortion of the diaphragm, air was admitted to the air-chamber and the pressure measured by means of a water manometer.

Large alterations in the level of liquid in the resonating tube were effected when desired by changing the pressure on the liquid contained in the reservoir and helix of copper tubing shown on the right in Fig. 1. The

[4] T. H. Gronwall, Phys. Rev. **30,** 71 (1927).
[5] K. Dorsing, Ann. d. Physik **25,** 227 (1908).
[6] W. Busse, Ann. d. Physik **75,** 657 (1924).

liquid flowed through a tube from the reservoir, through a needle valve and thence into the resonating tube through a small circular orifice drilled in the steel wall several centimeters above the diaphragm. When the liquid attained the desired height the needle valve was closed to prevent any variation in level during an experiment. Small variations in level were effected by means of a burette which was lowered into the open end of the resonating tube. The height of the column of liquid was measured by the jointed brass rod *A* attached to the scale *B* shown in Fig. 1. The rod had a sharp point on

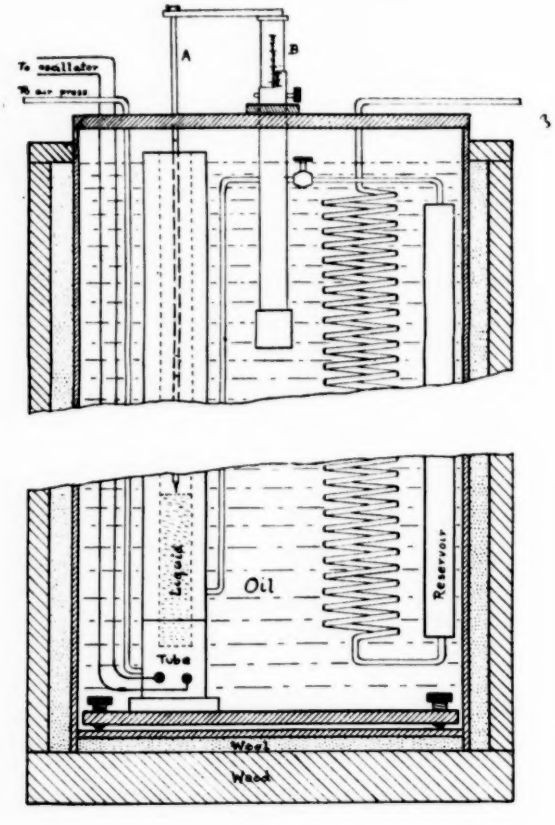

Fig. 1.

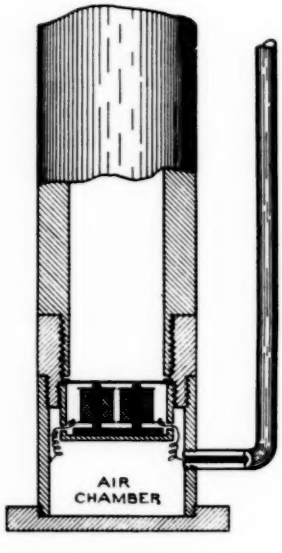

Fig. 2.

Diagram of apparatus.

the end which upon making contact with the liquid surface closed an electrical circuit thereby producing a signal in a set of head-phones. The scale *B* could be raised or lowered and vertical distances measured with a precision of 0.01 cm by the use of a vernier.

The oscillator, amplifier and detector are shown diagrammatically in Fig. 3. The oscillator was designed to produce a current whose frequency did not vary with small changes in the filament current, B-battery voltage, or variable output. To obtain a circuit with these properties a master oscillator

was used in which the oscillations were excited in the grid circuit and the current was so small that the coils and condensers did not change appreciably in temperature under operating conditions. The plate current in tube A (Western Electric Co., Type E) was approximately one milliampere and the B-voltage, 180 volts, was supplied by dry batteries. The master oscillator was transformer-coupled to the amplifier as shown. The tubes B_1 and B_2 were UX 212 Radiotrons operated from the lighting circuit. The B-voltage was obtained from the two voltage regulator tubes, Radiotron type UX 874, shown at D. The oscillating current now amplified to 90–100 milliamperes passed through the tuned filter circuit G. The intensity of the output current was regulated by the autotransformer E, and then passed through the telephone transformer F to the receiver at the bottom of the tube. The oscillator

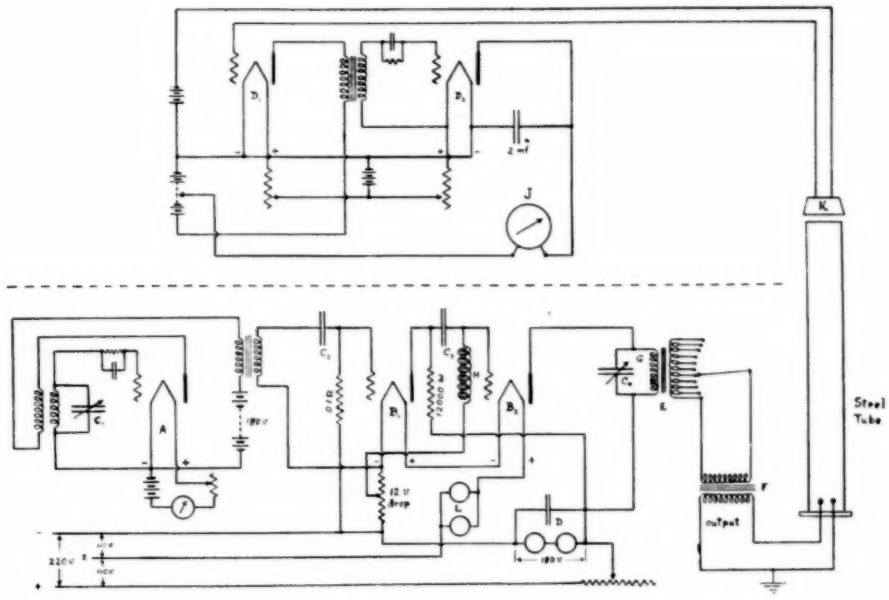

Fig. 3. Diagram of oscillator, amplifier and detector.

covered the range from 660–4500 cycles and the frequency remained appreciably constant throughout the whole range.

The oscillator was calibrated by obtaining the beat note between the current from the oscillator and the current produced in the coils of a telephone receiver by a toothed iron wheel (50 teeth) passing over the poles of the magnet. The shaft on which the toothed wheel revolved was geared (5-1) to a counter and any desired speed of rotation could be obtained by means of cone pulleys and a series resistance in the armature circuit of the motor. To measure the frequency the beat note was reduced to zero and held there and the time of 20,000 revolutions of the toothed wheel was measured with a stop watch. There was no difficulty in measuring the frequency with a precision of better than one tenth of one percent. The change in frequency produced by

varying the filament current of tube A by 0.05 amp. was not more than one part in two thousand and a variation of 4 volts in the B-battery did not show a detectable change in frequency.

The variable condenser C_1 consisted of a decade condenser, which could be varied in steps of 0.01 μf, in parallel with an air condenser filled with castor oil having a capacity of 0.012 μf. The frequency was determined at 10° and 90° on the scale of the air condenser and since the capacity varies linearly between these points the frequency could be determined for intermediate points by means of the relation

$$f=(b_1+xb_2)^{-1/2}$$

where

$$b_2=\frac{f_1^2-f_2^2}{(x_2-x_1)f_1^2f_2^2}$$

$$b_1=\frac{1}{f_2^2}-x_2b_2$$

and x_1 and x_2 are the readings on the condenser scale for the frequencies f_1 and f_2, respectively. This method reduced considerably the number of readings necessary to calibrate the oscillating circuit. The calibration was checked from time to time against a standard. This standard consisted of a fused quartz rod 91.5 cm long which was suspended in a horizontal position by two threads. A small armature of soft iron was cemented to one end of the rod with shellac and a telephone receiver with the diaphragm removed was mounted several millimeters away with the magnets facing the armature. The receiver was excited from the oscillating set and the resonance frequency for the fundamental longitudinal vibration of the rod, $3115.7\pm0.1\sim$, was checked against the condenser setting.

The frequency of maximum intensity for the sound waves emitted by the column of liquid in the tube could be determined by ear, but the detector shown in Fig. 3 was more satisfactory for the purpose and also furnished qualitative information regarding the shape of the resonance curves. A telephone receiver K used as a microphone was placed about one centimeter above the open end of the tube. The current generated by the sound waves was amplified by the tube D_1 which was transformer-coupled to the grid of D_2. In tube D_2 the grid was maintained at a positive potential by connecting it to the positive end of the filament and, therefore it acted as a rectifier. A minimum in the plate current as recorded by the D.C. microammeter J indicated a maximum in the intensity of the sound waves incident on the microphone. The same procedure was followed in determining the natural frequency of the diaphragm itself.

C. Diaphragms

It is necessary to investigate the vibrating system in detail in order to determine the relation between λ the wave-length, f the frequency and V the velocity of propagation of the sound waves in the tube. Lord Rayleigh[7] has

[7] Lord Rayleigh, Theory of Sound, Vol. II, p. 158 *et seq.*

shown that for the case of forced vibrations of a fluid contained in a circular cylinder the waves ultimately become plane if $\lambda \geqq 3.413\ R$, where R is the radius of the tube, and that if the source of vibration be symmetrical with respect to the axis the waves ultimately become plane for a smaller value of λ than the one given by the above expression. The condition for plane waves was amply satisfied in this investigation and the law of reciprocity permits us to consider the waves produced by the vibrations of the diaphragm as equivalent to the waves produced by the forced vibrations of a piston. The wave equation for this case has the form

$$\frac{d^2u}{dt^2} = V^2\frac{d^2u}{dz^2} + \frac{4}{3}\nu\frac{d^3u}{dz^2dt} \tag{1}$$

where u is the particle displacement, ν the kinematic coefficient of viscosity for the liquid and V represents the velocity of propagation in the tube. To determine the boundary conditions, G the bulk modulus of the liquid is defined by the equation $G=\rho V^2$, where ρ is the density of the liquid. The axis of z coincides with the axis of the tube; for the diaphragm $z=0$ and for the surface of the liquid $z=l$.

The boundary conditions for the propagation of a longitudinal wave along the axis of the tube require that at the free surface of the liquid the sum of the elastic and viscous stresses parallel to z vanish, namely,

$$G\frac{du}{dz} + Q\rho\frac{d^2u}{dzdt} = 0 \qquad \text{for } z=l; \tag{2}$$

and that at the surface of the liquid in contact with the diaphragm the pressure must be equal on the two sides, hence

$$\pi_0 e^{int} = Ku + m\frac{d^2u}{dt^2} + G\frac{du}{dz} + Q\rho\frac{d^2u}{dzdt} \quad \text{for } z=0, \tag{3}$$

where $Q=4\nu/3$; K is the stiffness per unit area and m the effective mass per unit area of the diaphragm and π_0 is the amplitude of the pressure. The displacement at all points in the system varies harmonically with the time and

$$u = A_1 e^{int+(\alpha+i\beta)z} + A_2 e^{int-(\alpha+i\beta)z} \tag{4}$$

will be a solution of (1), where

$$\alpha = \frac{1}{2}\frac{n^2Q}{V^3}$$
$$\beta = \frac{n}{V} \tag{5}$$

provided n^2Q^2/V^4 is small compared with unity. The constants A_1 and A_2 are to be evaluated from the equations expressing the boundary conditions at $z=0$ and $z=l$.

From Eqs. (1) to (4) the following equation for the displacement u_l at the surface of the liquid can be found without trouble

$$|u_l|^2=\frac{\pi_0^2}{(M^2+P^2)\left\{\left(\frac{1}{4}\frac{n^4l^2}{V^4}+Nl\right)Q^2+\cos^2(\phi-\epsilon)\right\}} \tag{6}$$

where

$$M=n\rho V,\quad P=K-mn^2,\quad N=\frac{P}{P^2+M^2}\cdot\frac{1}{2}\cdot\frac{n^4\rho}{V^4}$$

$$\phi=\beta l=\frac{n}{V}l,\qquad \epsilon=\text{arc tan}\frac{M}{P}$$

Consider now the case of resonance $|u_l|^2=\max$. Neglecting for the moment the term in Q^2 in the denominator on the right hand side of Eq. (6), $|u_l|^2$ will be a maximum when $\cos(\phi-\epsilon)=0$, i.e. when

$$\phi-\epsilon=m\pi-(\pi/2)$$

where m is the number of half waves in the tube. For resonance, therefore, the relation between V, l and the resonance frequency of the system will be

$$f=\frac{V}{2l}(m+\eta) \tag{7}$$

or

$$V=\frac{2l}{T(m+\eta)} \tag{8}$$

where $T=1/f$, and

$$\eta=\frac{\epsilon}{\pi}-\frac{1}{2}=\frac{1}{\pi}\left\{\text{arc tan}\frac{n\rho V}{K-mn^2}\right\}-\frac{1}{2}. \tag{9}$$

At the resonance frequency of the diaphragm $K-mn^2=0$, hence $\eta=0$, and

$$f_0=\frac{V}{2l}m=\frac{V}{\lambda} \tag{10}$$

where f_0 is the resonance frequency of the diaphragm when clamped in the holder.

The effect of the term in Q^2 in shifting the maximum of $|u_l|^2$ represents the effect of viscosity on the resonance frequency of the system. It can easily be shown that this shift of the resonance frequency is but a fraction of the width of the resonance curve at half maximum. In the present experiments this corresponds to less than one cycle.

In the above discussion the give of the walls of the tube is ignored, but for the purpose in view Eq. (10) is nevertheless, sufficiently accurate. It is evident that f_0 is the frequency at which the measurements are best taken. for in this case, and in this case only, does the simple relation $V=\lambda f$ apply.

In the absence of sufficient knowledge regarding the constants of the diaphragm only qualitative information can be obtained from Eqs. (8) and (9). Fortunately, however, this information is sufficient to allow Eq. (10) to be tested experimentally. The manner in which V varies with T in Eq. (8) is shown in Table I where $T_1>T_0>T_2$.

TABLE I.

Period	$P=K-mn^2$	$\epsilon=\arctan M/P$	η	V
T_1	positive	$\epsilon<\pi/2$	negative	$V_1>V$
T_0	0	$\epsilon=\pi/2$	0	$V_0=V$
T_2	negative	$\epsilon>\pi/2$	positive	$V_2<V$

In the preliminary experiments to test Eq. (10) two diaphragms D_1 ($f_0=1269\sim$) and $D_2(f_0=2590\sim)$ were investigated over a wide range of frequencies. The relation between the height of the column of liquid $l(=\lambda/2)$ and the period for resonance is shown in a much exaggerated form by the curves in Fig. 4. The exaggeration is necessary as the curve is nearly a straight line throughout its entire length except near the extremities.

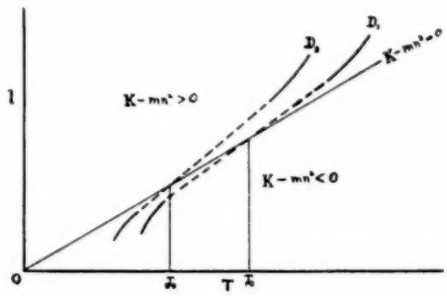

Fig. 4. Relation between height of the column of liquid and the period of resonance.

Inspection of these curves shows that they are in accord with the results predicted in Table I. It may also be observed that the tangents to the curves at the point for which $T=T_0$ pass through the origin; this is in agreement with Eqs. (8) and (9) as can easily be shown.

TABLE II.

Diaphragm	f_0	$\lambda/2$	$V=\lambda f$
D_1	1269	57.53 cm	1460 m/s
D_2	2590	28.07	1455

The observations which determine the shape of the curves in Fig. 4 were taken at the same temperature and with the same tube in both cases,

so that a comparison of the diaphragms can be made without requiring a correction for temperature or for the yielding of the walls of the tube. The observed data for $f=f_0$ and the calculated values of V are given in Table II.

A further experimental test of the equations is possible when the height of the column of liquid in the tube corresponds to several half wave-lengths. From Eq. (8) it is seen that unless $\eta=0$; $l_1=\lambda/2$, $l_2=\lambda$, and $l_3=3\lambda/2$ will not be in the ratio 1:2:3, since there will not be an integral number of half waves in the tube. Hence, the values of V obtained from l_1, l_2 and l_3 should differ as m takes on successive integral values. A typical set of curves for this case is shown in Fig. 5 and Table III contains the data from another experiment of this type made with diaphragm D_2.

TABLE III.

m	f_0	l	$\lambda/2$	Av. $\lambda/2$
1	2590	28.07 cm	28.07 cm	
2	2590	56.30	28.15	28.12 cm
3	2590	84.40	28.13	

D. Method of Experimentation and Treatment of Data

The procedure followed in making a complete run on a given liquid was as follows:

1. The tube was placed in position, (see Fig. 1), the point of contact between the diaphragm and the measuring rod was determined and the reading on the vertical scale recorded.

2. The natural frequency f_0 of the diaphragm was determined by the method described under B.

3. The variable condenser in the oscillating set was adjusted for a frequency slightly higher than f_0 and the liquid admitted to the tube until the resonance height, $l=\lambda/2$, was reached.

4. The system was then left undisturbed for about 10 minutes to make certain that thermal equilibrium was established and the resonance frequency was then carefully determined and the height of the column of liquid measured.

5. Several cc of the liquid were then withdrawn from the tube and the resonance frequency was again determined and the new height measured.

6. This process was continued until four or five determinations had been made for frequencies slightly above and below f_0.

7. In the investigation of diaphragms the procedure described in 3 to 6, corresponding to the resonance height $l_1=\lambda/2$, was then repeated for $l_2=\lambda$ and $l_3=3\lambda/2$.

The results of these experiments were then used as follows:

1. From the vertical heights recorded for contact between the measuring rod and the surface of the liquid the different lengths of the column were determined.

2. The condenser readings were expressed as reciprocals of the frequency.

3. A curve was plotted using the height of the column of liquid as ordinate and the period of vibration as abscissa.

4. The point corresponding to the natural period of the diaphragm was located on the curve and the height of the column at this point determined.

5. The velocity of propagation of the longitudinal waves in the liquid was then calculated from Eq. (10).

A typical set of curves for l_1, l_2, and l_3 plotted in accordance with the above method are shown in Fig. 5. The points indicated by the circles represent the experimental observations.

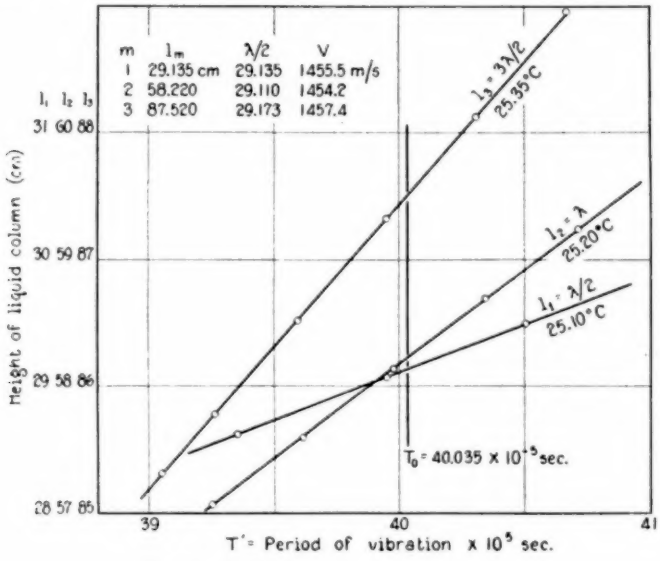

Fig. 5. Typical curves for l_1 l_2 and l_3.

E. The Gronwall Correction Formula

The correction formulas of Korteweg and Lamb assume that the liquid completely fills the tube, thus introducing a requirement which in the present investigation would obviously be quite inconvenient to fulfill. Gronwall, however, considers the case where the liquid under observation only partly fills the tube, while the tube itself is supposed to be in a tank filled with another liquid, as would be the case when the tube is placed in a constant temperature bath.

The boundary conditions can all be satisfied experimentally, including that for the surface of separation between liquid and diaphragm, viz. $p=0$ at $z=0$ (reference 4, Eq. (31)), which is automatically satisfied for f_0 the natural frequency of the clamped diaphragm, except for the small viscous stress $Q\rho\ (d^2u/dzdt)$. Gronwall's results show that B the observed velocity of the longitudinal waves in the liquid as obtained from Eq. (10) is related to V_0 their velocity in an unlimited body of the liquid by the equation

$$V_0=\frac{V}{1-\delta} \tag{11}$$

where

$$\delta = y + 2y^2 + \left(7 - \frac{\pi^2}{3}\right)y^3 + \left(30 - \frac{7\pi^2}{3}\right)y^4 + \cdots$$

For thick walled tubes

$$y = \frac{\rho V^2}{E}\left(\frac{b^2+a^2}{b^2-a^2} + \sigma\right) \tag{12}$$

and for thin walled tubes

$$y = \frac{\rho V^2}{E}\left[\frac{2}{3}\left(\frac{b^2+a^2}{b^2-a^2} + \sigma\right) + \frac{1}{3}\left(\frac{1}{2\sigma} - 1\right)\frac{a}{b-a}\right] \tag{13}$$

where ρ is the density of the liquid, E and σ are Young's modulus and Poisson's ratio, respectively, for the material of the tube and a and b are the inner and outer radii.

The correction for the elasticity of the walls of the tube given by Eq. (11) was investigated for three tubes made of mild steel by the extrusion process. The dimensions are given in Table IV. The correction factors for the different tubes were computed, taking E for mild steel as 2.08×10^{12}

TABLE IV.

Tube	a	b	$b-a$	$1/1-\delta$
I	1.945 cm	3.185 cm	1.240 cm	1.0285
II	1.938	2.225	0.287	1.0771
III	2.024	2.160	0.136	1.1675

dynes/cm^2 and σ as 0.3. The quantity y was obtained from Eq. (12) for tubes I and II and from Eq. (13) in the case of tube III. A comparative analysis of an experiment with the three tubes containing air-free distilled water, using the same diaphragm and $l = \lambda/2$ is given in Table V. The diaphragm holder, Fig. 2, was so constructed that the tube did not come in contact with the diaphragm, hence, changing the tube did not alter the clamping at the boundary and f_0 was the same in each case.

TABLE V.

Tube	V (Eq. (10))	V (Correct.)	Temp.	V at 25°C[8]
I	1453.4 m./s.	1494.8 m./s.	24.8°C	1495.6 m./s.
II	1384.9	1491.7	25.6	1489.8
III	1277.6	1491.6	24.85	1492.1

The agreement between the calculated velocity of sound in the three tubes when corrected by Gronwall's formula is very good, but thin tubes require such a large correction that an appreciable error may be introduced

[8] The temperature corrections have been made from a least square solution applied to forty observations taken between 23° and 30°C on air-free distilled water.

by uncertainty in the value of E, consequently tube I and two shorter tubes of the same dimension were used.

F. The Ascoloy Tube

In the measurements made with tube I great difficulty was encountered from rusting and freshly distilled water showed traces of rust after having been in the tube for several hours at 25°C. When measurments were made at high temperatures it was necessary to keep the water in the tube over a period of many hours and the rusting became so serious that steps were taken to prevent it. The difficulty was finally overcome by chromium plating the diaphragm and by making a new tube of approximatly the same dimensions from a stainless steel manufactured by the Allegheny Steel Co. under the trade name of Ascoloy 22. This tube had the dimensions $a=1.945$ cm, $b=3.155$ cm, $b-a=1.210$ cm, length 40 cm, $E=1.97\times10^{12}$ dynes/cm^2 and $\sigma=0.3$. The tube was designed for observations on $l=\lambda/2$ and since only a slight variation in the level of the liquid was required, the small hole in the wall was eliminated. In the new tube (tube V) the liquid was introduced through the open end and small changes in level were effected with the burette.

Tube V showed no signs of corrosion even with the most concentrated salt solution, but the calculated value of V for air-free distilled water was about 1/2 of one percent lower than the value previously obtained using tube I. Careful investigation showed that this difference in the value of V could only be explained by the influence of the hole in the wall. To test this point a small steel plug was made which just filled the hole and observations were taken with the plug in and then with it out. A definite lowering in the value of V was observed when the hole was plugged. Four sets of readings gave an average lowering of 6.2 m./s. and a new tube without a hole made from tube I gave results which agreed with those obtained from tube V within the limits of precision.

G. Results

Following the method outlined above the velocity of sound was measured in air-free distilled water at 25°C and from 30° to 70°C at intervals of ten degrees, and in solutions of NaCl and KCl for different concentrations at 25°C.

Table VI.[9]

Diaphragm	Thickness	Res. Freq.	No. of Read's.	Av. Vel. at 25° C.
D_1	0.031 cm	1269	3	1498.0 m./s.
D_2	0.0505	2590	15	1494.2
D_3	0.048	2318	4	1494.8
D_4	0.052	2715	6	1492.5
		Height of Column	No. of Read's.	Av. Vel. at 25°C.
		$\lambda/2$	20	1492.2 m./s.
		λ	14	1493.1
		$3\lambda/2$	10	1494.1

[9] The values of V in Table VI have not been corrected individually for the effect discussed in Section F.

1. Air-free distilled water. The value of V for air-free distilled water obtained with four different diaphragms at their respective resonance frequencies and with the same diaphragms, D_1 excepted, for $l=\lambda/2, \lambda, 3\lambda/2$ are given in Table VI.

The average of 47 observations on tube I with air-free distilled water at 25°C gave for the velocity of sound 1493.2 m./s. Correcting this value for the effect of the hole discussed under Section F and including 5 additional observations made with tube V gives for the velocity of propagation of the longitudinal waves in an unlimited body of the liquid

$$V_0=1485.4\pm 2.3 m/s.^{10}$$

From this value of V_0 and the relation $G=\rho V_0^2$ we can obtain the bulk modulus and the adiabatic compressibility of water.

$$G=2.2000\times 10^{10} \text{ dynes/cm}^2.$$

$$\kappa=1/G=4.5455\times 10^{-11} \text{ cm}^3/\text{dyne}.$$

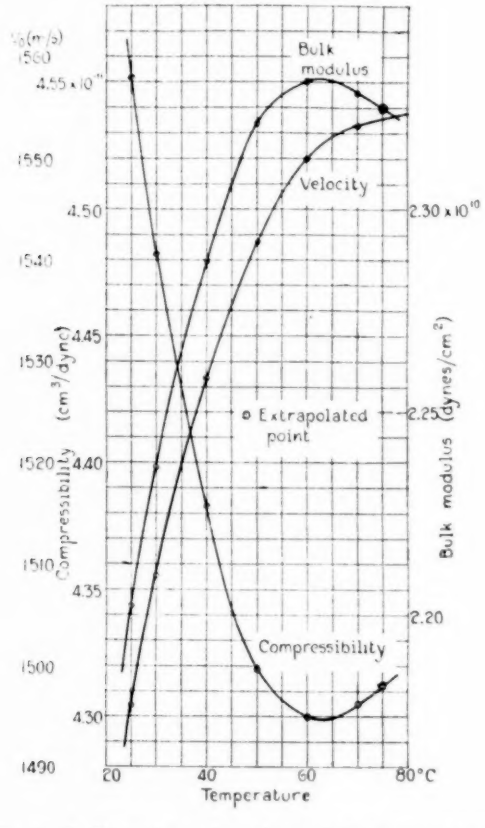

Fig. 6. G, V_0 and κ as functions of the temperature.

[10] L. G. Pooler, Phys. Rev. **31,** 157 (1928). In a note presented at the Chicago meeting of the Physical Society in Nov. 1927 the value was given as 1493.2 m/s. The effect of the hole in the wall of tube I was subsequently discovered.

Measurements on the velocity of sound, bulk modulus and compressibility at different temperatures taken from two experiments using tube I in which the agreement between corresponding values of V_0 was remarkably

TABLE VII.

Temp.	Av. V_0	G	κ
25°C	1486.0 m./s.	2.2018×10^{10} dynes/cm²	4.5417×10^{-11} cm³/dyne
30	1498.7	2.2362	4.4716
40	1518.3	2.2872	4.3721
50	1531.6	2.3208	4.3088
60	1539.8	2.3311	4.2898
70	1543.1	2.3284	4.2947
Extrapolated point			
75	1544.2	2.3248	4.3014

close are given in Table VII. The curves in Fig. 6 have been plotted from these data and exhibit the variation of the measured quantities with the temperature.

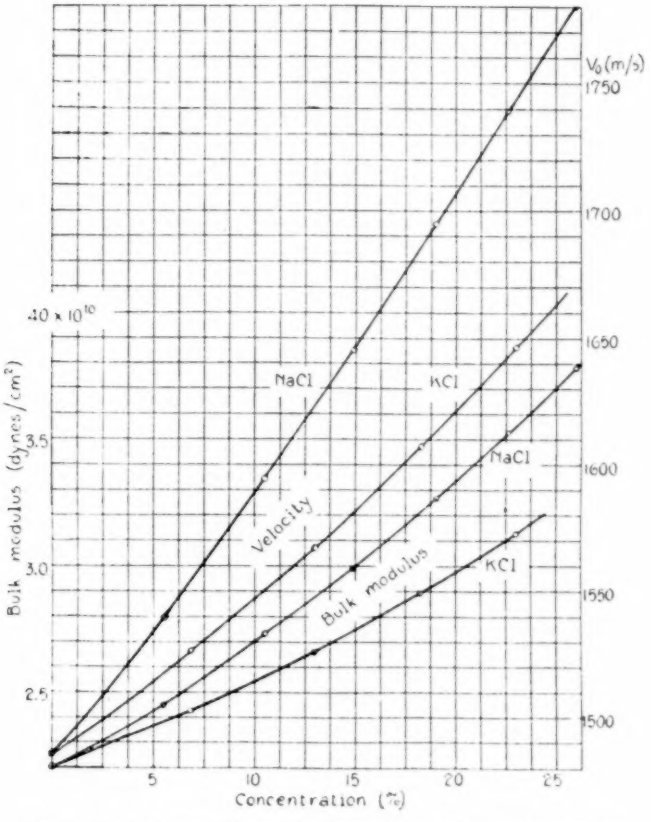

Fig. 7. Variation of V_0 and bulk modulus with concentration.

Above 70°C the column of liquid could not be maintained in a state of vibration long enough to permit taking the necessary observations. This

phenomenon was apparently caused by the liquid boiling under reduced pressure as bubbles of gas could be seen adhering to the walls of the tube below the surface. When they were removed by stirring the liquid column came into resonance only to cease again in a very abrupt manner after several minutes.

2. Salt solutions. The velocity of sound was measured in aqueous solutions of NaCl and KCl for different normalities up to saturation using tube *V*. The results are given in Table VIII and the curves in Fig. 7 illustrate the variation in V_0 and the bulk modulus with the concentration.

TABLE VIII.

Concentration			Density	V_0 at 25°C	G	κ
NaCl	1N	5.5%	1.036	1539.4 m/s.	2.455×10^{10} dy./cm^2	4.073×10^{-11} cm^3/dy.
	2N	10.5	1.072	1593.8	2.723	3.672
	3N	14.9	1.105	1644.8	2.989	3.345
	4N	19.0	1.137	1695.1	3.267	3.061
	5N	22.6	1.165	1739.6	3.526	2.837
	6N	26.0	1.194	1780.1	3.784	2.643
KCl	1N	6.9	1.041	1526.5	2.426	4.123
	2N	13.0	1.081	1567.7	2.657	3.764
	3N	18.3	1.119	1607.7	2.892	3.458
	4N	23.0	1.151	1647.2	3.123	3.202

H. Discussion

The results obtained with air-free distilled water indicate that the method is one of high precision for the measurement of the velocity of sound in liquids and solutions and that much valuable information can be gained regarding the bulk modulus and the compressibility. The coefficient of viscosity enters into Eq. (6), but due to the excessively complicated relation which must exist at the boundary between the liquid and the tube it is doubtful if any information regarding it can be obtained from experiments of this type. It is felt that the limits of precision of this method have not as yet been reached and that with some further small refinements to the apparatus, the value of the velocity of sound can be measured to better than one tenth of one percent.

Recently two papers by Hubbard and Loomis[11] have appeared which present the results of an experimental determination of the velocity of sound in liquids at high frequencies (around 500,000~). The precision of their measurements is extremely high and they find that at the frequencies used the effect of the yielding of the walls of the tube can be completely neglected. The results of the present investigation correspond closely with theirs as regards the shape of the velocity-temperature curve and the velocity-concentration curves, but the measurements at audio frequencies are in all cases about one percent lower than at 500,000~. They were unable to obtain satisfactory readings at supersonic frequencies above 40°C while

[11] Hubbard and Loomis, Phil. Mag. **5**, 1177 (1928); Loomis and Hubbard, J.O.S.A. **17**, 295 (1928).

in the present investigation it was possible to continue observations up to 70°C before the column of liquid ceased to resonate. This difference can easily be explained when it is recalled that in a longitudinal wave the variation in pressure at a node is proportional to the frequency, and hence in their experiments ebullition would commence at a lower temperature.

The position of the maximum in the curve for the bulk modulus and the corresponding minimum in the compressibility curve at 63°C shown in Fig. 6 is in good agreement with the temperature found by other experimenters using entirely different methods. This peculiar behavior of the compressibility is fully discussed from the thermodynamical aspect in a paper by Bridgman[12] in which experiments with water at different temperatures and under static pressures up to 1200 kg/cm^2 are described.

The progress of this research indicates that many interesting facts can be discovered from measurements on the velocity of sound in liquids and particularly in solutions. It is hoped that through further experiments of this kind it may be possible, in the near future, to throw some light on the subject of dissolved substances in general and to derive an expression for the relation between the compressibility and the diminution in volume which occurs when many substances dissolve. The method also lends itself to a study of the rate of chemical reaction for cases in which the velocity of sound differs for the reacting liquids and the product of the combination.

The writer wishes to express his appreciation of the kindness of Dr. Wente and the late Dr. I. B. Crandall of the staff of the Bell Telephone laboratories who furnished the thick diaphragms used in these experiments and to Professor Colin G. Fink in whose laboratory the diaphragms were chromium plated; and also to acknowledge his indebtedness to Professor A. P. Wills whose advice and encouragement have been of great assistance during the progress of this research.

[12] P. W. Bridgman, Proc. Amer. Acad. of Arts & Sci. **48**, 309 (1912).

THE DIELECTRIC CONSTANT AND THE MOLECULAR STRUCTURE OF CS_2

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(Received February 20, 1930)

Abstract

By the radio frequency heterodyne method previously developed measurements have been made of the dielectric constant of CS_2 at various pressures and temperatures. The molecular polarization is shown to be independent of temperature and therefore the electric moment is zero. The previous value published tentatively is shown to be in error. The structure of the CS_2 molecule can now be considered to be rectilinear and symmetrical. The value for the molecular polarization obtained is $P = 22.36$.

Comparisons with other data are given, and some convenient modifications in the experimental method and in the interpretation of dielectric constant data are described.

IN A recent article of this review Dr. J. B. Miles together with the author[1] gave values for the dielectric constant and the electric moment of CO, COS, CS_2, and H_2S. The results then obtained indicated a small electric moment for the CS_2 molecule which seemed to be in contradiction to Williams'[2] results from the study of solutions. The experiments on CS_2 were accompanied by two chief difficulties. First, the apparatus was not adapted to the study of hot vapors, since part of the gas system was always at room temperature and it was therefore possible to work only at pressures below about one-third of an atmosphere. Secondly, the solubility of the CS_2 in the small amount of grease collected around the stopcocks made the results on CS_2 somewhat questionable. For these reasons the values for CS_2 were given only tentatively in the above mentioned article and it was there promised to make more conclusive measurements in the near future. Since then the apparatus has been adapted to work with hot vapors by Dr. J. B. Miles in collaboration with the author, and measurements have been made on CS_2 under excellent experimental conditions.

While this work was in progress there appeared an article by Ghosh, Mahanti, and Mukherjee[3] on the dielectric constant and the molecular structure of CS_2 and N_2O, in which the moments of CS_2 and N_2O were found to be zero. The experiments described in the present article verify the conclusion that CS_2 has no appreciable electric moment but the value of the molecular polarization obtained is not in sufficiently close agreement with that of the above mentioned observers. It therefore seems worth while to give a full discussion of the present work.

[1] C. T. Zahn and J. B. Miles, Jr., Phys. Rev. **32,** 497 (1928).
[2] J. W. Williams, Phys. Zeits. **29,** 177 (1928).
[3] P. N. Ghosh, P. C. Mahanti, and B. C. Mukherjee, Zeits. f. Physik **58,** 145 (1929).

Experimental Method and Modifications

The radio frequency heterodyne null method was used as previously described and applied to the measurement of a considerable number of gaseous substances.[4] In the present arrangement of the apparatus there is one stopcock, which is separated from the gas system by liquid CS_2 in the manometer described,[4] and should therefore not be so likely to introduce impurities even if grease were used in the seal. In order to make perfectly certain of this the grease was replaced by P_2O_5. The CS_2 used was taken from the same purified specimen as used before.[1]

Some convenient modifications have been made in the method of interpretation of the dielectric constant data as follows. The dielectric constant should obey Debye's equation:

$$3\left(\frac{\epsilon-1}{\epsilon+2}\right)vT=AT+B$$

where ϵ is the dielectric constant, v is the specific volume referred to the *ideal* volume under S.P.T. conditions, T is the absolute temperature, and A and B are constants.

$$B=\frac{4\pi N_0}{3k}\mu^2 \text{ or } \mu=1.099_8\times10^{-18}B$$

where N_0 is Loschmidt's number, the ideal number of molecules per cc under S.P.T. conditions, $2.705_6\times10^{19}$, k is Boltzmann's constant, $1.370_9\times10^{-16}$, and μ is the electric moment of the molecule.

In previous experiments it has been customary to determine the difference between the dielectric constants at atmospheric pressure and at approximate vacuum, and to determine the value of v by the van der Waal equation in its approximate form:

$$v=\frac{RT}{p}\left\{1-\frac{(a/vp)-b}{v}\right\}$$

using for v on the right hand side its approximate or ideal value RT/p. This method of calculation is convenient if the dielectric constant is measured at only one pressure. A more satisfactory way to determine $(AT+B)$ is to make measurements of $\Delta\epsilon$ over the whole range of pressure available, and at the same time to test the Clausius-Mossotti relation: $(\epsilon-1)/(\epsilon+2)::$ density. At a fixed temperature the polarization would be accurately proportional to p only for an ideal gas so that plotting $3(\epsilon-1)/(\epsilon+2)$ against p would not give a straight line. If we plot against p', the *ideal* pressure which the gas would have at the given temperature and density, we should obtain a straight line of slope $3[(\epsilon-1)/(\epsilon+2)]\,V/R\,T$. The value of p' can be

[4] C. T. Zahn, Phys. Rev. **24,** 400 (1924); C. P. Smyth and C. T. Zahn, Jour. Amer. Chem. Soc. **47,** 2501 (1925); C. T. Zahn, Phys. Rev. **27,** 329 (1926); C. T. Zahn, Phys. Rev. **27,** 455 (1926); C. T. Zahn and J. B. Miles, Jr., Phys. Rev. **32,** 497 (1928); J. B. Miles, Jr., Phys. Rev. **34,** 964 (1929).

calculated as follows. Van der Waal's equation can be rewritten approximately:

$$v=\frac{1}{\frac{p}{RT}\left\{1+\frac{p}{RT}\left(\frac{a}{RT}-b\right)\right\}}\equiv\frac{RT}{p'}$$

which defines:

$$p'=p\left\{1+\frac{p}{RT}\left(\frac{a}{RT}-b\right)\right\}.$$

Hence the effect of the van der Waal constants is to introduce into the actual pressure relation a small quadratic term which can be taken into account by plotting against p' as above mentioned. The final value of $(AT+B)$ is got by multiplying the slope by RT^2. This is done for a range of temperatures and the values plotted against T. The resulting straight line gives A as the slope and B as the intercept from which the moment is determined. If the molecule studied has no fixed moment then the values of $3(\epsilon-1)/(\epsilon+2)$ v should be constant, and it is not necessary to draw the Debye line in order to determine A. It is only necessary to average the experimental values of $3[(\epsilon-1)/(\epsilon+2)]v$, which are approximately equal for the different temperatures used.

The above method of plotting has another advantage as follows. In a previous paper the author has mentioned the fact that it is impossible to make a reading for the dielectric constant at vacuum because the condenser plates are then so perfectly insulated thermally that a small but very disturbing temperature difference can be set up between them. It is then necessary to extrapolate to vacuum in order to find the actual value of($\epsilon-1$). The apparatus can always be so adjusted that the difference values of $(\epsilon-1)$ are approximately the actual values. These values can be divided by the corresponding approximate values of $(\epsilon+2)$ and then $3\{\Delta(\epsilon-1)/\epsilon+2\}$ can be plotted against p'. The linear extrapolation should be very accurate since the correction due to the factor $(\epsilon+2)$ is usually small and, in fact, often negligible. It is easily seen that the factor $\epsilon+2$ has the effect of introducing a small quadratic term in the value of $\epsilon-1$ as a function of the pressure since

$$3\left\{\frac{\epsilon-1}{\epsilon+2}\right\}::p' \text{ or } (\epsilon-1)::p'\left(1+\frac{\epsilon-1}{3}\right)$$

and $(\epsilon-1)$ on the right hand side may be set proportional to p' approximately.

For a considerable number of gases there seems to be no question concerning the validity of the Clausius-Mossotti relation. On the other hand there have been performed a number of experiments[5] in which anomalies

[5] M. Jona, Phys. Zeits. **20,** 14 (1919); C. T. Zahn, Phys. Rev. **27,** 329 (1926); K. Wolf, Phys. Zeits. **27,** 588, 830 (1926); K. Wolf, Ann. d. Physik **83,** 884 (1927); F. Maske, Phys. Zeits. **28,** 533 (1927); J. B. Miles, Jr., Phys. Rev. **34,** 964 (1929).

have occurred, particularly in the case of vapors near the condensation point. These anomalies have been attributed to two causes, association and actual condensation on the condenser plates. The author has performed experiments to show that both these effects exist; for example, for water vapor. In the case of water vapor condensation on the condenser plates is accompanied by electrical conductivity which can be measured directly. The existence of such effects, whether they be due to association or condensation, or both can be detected by pressure curves such as those described above. If they are found to exist they can usually be eliminated by working at sufficiently low pressures.

TABLE I.

$T°K$	p cm Hg	p' cm Hg	$3\left\{\frac{\Delta(\epsilon-1)}{\epsilon+2}\right\}\times 10^6$	$3\left\{\frac{\epsilon-1}{\epsilon+2}\right\}\frac{10^6}{p'}$	$3\left\{\frac{\epsilon-1}{\epsilon+2}\right\}v\times 10^6$	P
325.1$_1$	14.21	14.25	477	from curve		
	25.33	25.44	835			
	34.42	34.63	1134			
	44.47	44.82	1479			
	53.72	54.23	1779			
	64.49	65.23	2147			
	64.57	65.31	2149			
	53.76	54.27	1782			
	43.82	44.16	1454			
	34.96	35.18	1143			
	24.37	24.48	793			
	15.92	15.96	494	2518	2997	
391.7$_6$	15.21	15.23	305			
	28.93	29.03	697			
	48.81	49.09	1247			
	50.27	50.57	1264			
	30.40	30.51	748			
	15.81	15.84	330	2088	2995	
489.2$_2$	14.64	14.66	385			
	22.63	22.67	558			
	33.45	33.53	787			
	43.06	43.19	983			
	52.95	53.15	1199			
	61.71	61.98	1384			
	52.95	53.15	1199			
	43.37	43.50	987			
	33.81	33.89	763			
	24.35	24.39	541			
	15.00	15.02	334	1666	2985	
322.3$_1$	13.69	13.72	618			
	24.16	24.26	964			
	33.37	33.57	1284			
	43.26	43.60	1614			
	52.87	53.37	1942			
	62.15	62.85	2264			
	53.13	53.63	1957			
	43.54	43.88	1618			
	33.47	33.67	1286			
	24.10	24.20	958			
	14.15	14.18	633	2538	2995	
					2993, mean	22.36

Experimental Results

In the present measurements on CS_2 complete pressure curves were obtained at four different temperatures in order to insure the absence of such effects. In Table I are shown the experimental values obtained. The fourth column contains the difference readings, $3[\Delta(\epsilon-1)/(\epsilon+2)]$, referred to a fixed point of the experimental condenser system for convenience

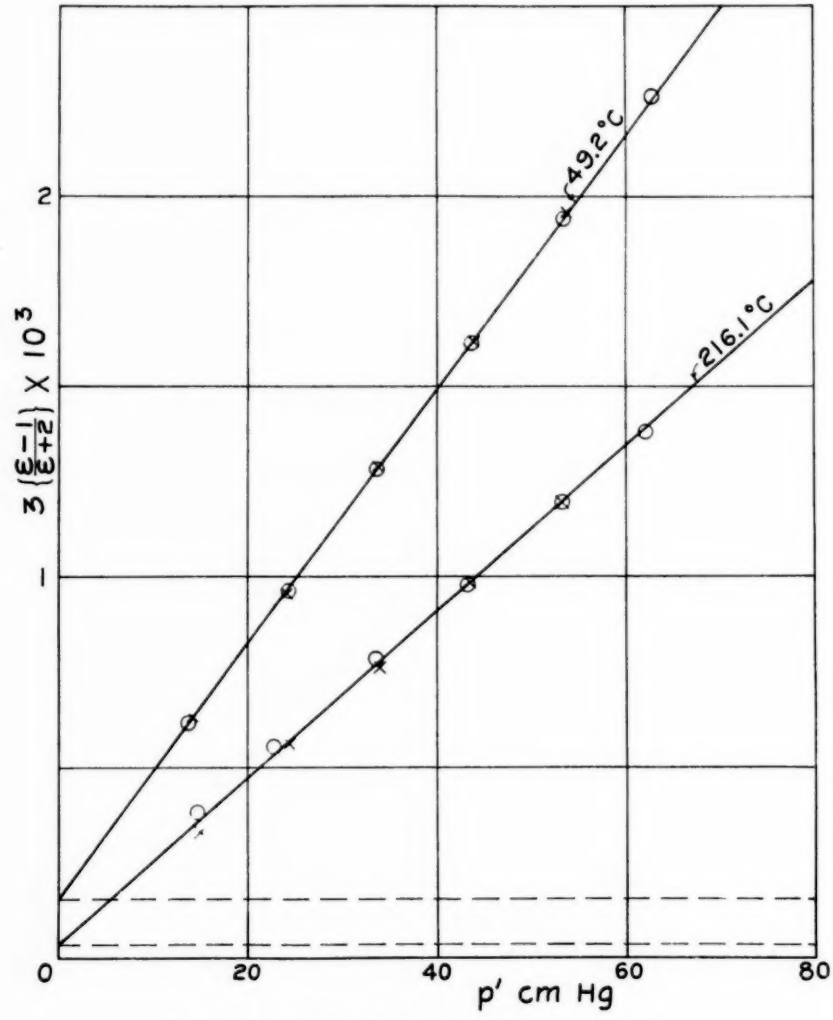

Fig. 1. Variation of polarization with pressure, p'.

in the calculations. The circuits are always adjusted to give the vacuum reading at approximately this fixed point, so that there is no appreciable error introduced in the value of the slope of the pressure curves. A table of calculated values or an accurately drawn chart then serves to facilitate the calculations of ϵ. The true values of $3\{\epsilon-1/\epsilon+2\}$ are measured from the zero values obtained by extrapolation on the curves. In Fig. 1 the values

of $3[\Delta(\epsilon-1)/(\epsilon+2)]$ are plotted against p' and the true values are measured from the horizontal zero lines. For the calculation of p' values of the van der Waal constants were obtained from Kaye and Laby: $a=0.02316$ and $b=0.00343$. Only two of the four sets of data are plotted here for illustration, the best and the worst. The pressure runs were always repeated in the reverse direction in order to eliminate the effect of errors caused by any drifts in the condenser system not due to the CS_2. The part of the readings for increasing pressure is marked by circles; and the part for decreasing pressure, by crosses. The line for the temperature 49.2°C is remarkably well reproduced, while that for 216.1°C shows a slight drift, which is eliminated in the drawing of the line. The strict linearity of these pressure curves indicates that there is no appreciable association or surface condensation throughout the total observed range of pressure.

The last column of Table I contains the value of the molecular polarization. P, or the total induced electric moment per gram-molecule of the substance, calculated from the mean value in the preceding column. $(\epsilon-1)/(\epsilon+2)v$ is the moment or polarization due to N_0 molecules; therefore P can be obtained from the values in the sixth column as indicated by:

$$P=(n/3N_0)\times 3\{\epsilon-1/\epsilon+2\}v=7.4716\times 10^3\times 3\{\epsilon-1/\epsilon+2\}v$$

where n is Avogadro's number, $6.064_4\times 10^{23}$. The values of the constants, n, N_0, L, and k used in these calculations are those given by Birge.[6]

Since the values in the last two columns of Table I are independent of temperature within the limits of experimental error, as mentioned above it is not necessary to draw a Debye line in order to determine the constant A. The results can be summarized by: $A=0.002993$ or $P=22.36$, and $\mu=B=0$.

Comparisons with Other Data

The result $\mu=0$ is in accord with the observations of Ghosh, Mahanti, and Mukherjee,[4] but the value of A given by them is 0.002912, about three percent lower than the above value. The discrepancy may be due to a calibration error in either of the two sets of experiments. It is believed by the author that the calibration of the apparatus used for the measurements given here is accurate to a fraction of a percent. Evidence substantiating this has been pointed out by Stuart[7] and by the author.[8] Furthermore the value of A for air given by the above mentioned authors is 0.0005797, about one percent higher than that obtained by the author,[9] 0.000572, and deviates in the opposite direction to that required to explain the discrepancy in the values for CS_2. A part, if not all, of the deviation could be explained by the failure of the above mentioned authors to take into account the departures of the gas from the ideal law. At atmospheric pressure this amounts

[6] R. T. Birge, Phys. Rev. Supplement, **1**, 1 (1929).
[7] H. A. Stuart, Zeits. f. Physik **47**, 457 (1928).
[8] C. T. Zahn and J. B. Miles, Jr., Phys. Rev. **32**, 497 (1928).
[9] C. T. Zahn, Phys. Rev. **24**, 400 (1924).

to about two percent in such a direction as to increase the values given. Their values of $(\epsilon-1)$ agree remarkably well for different temperatures, but if they worked at approximately constant density of gas the above mentioned correction would probably not sensibly alter this agreement. In addition there is an unimportant error of a small fraction of a percent introduced by the neglect of the factor $(\epsilon+2)$. They also give the value of $n^2_\infty = 1.002956$, taken from Graetz's handbook which is *higher* than their value $\epsilon = 1.002912$. Now deviations between n_∞^2 and ϵ are usually in the opposite direction[10] because the extrapolation to n_∞ is usually done from the visible spectrum neglecting the infra-red terms which have been shown to be of importance in the case of CO_2. In the case of CO_2 the refractivity has been measured over the entire range from the ultra-violet through the infra-red. Fuchs[11] has extrapolated for n_∞^2 taking into account the infra-red terms and obtains a value differing from the author's value of ϵ by less than one-tenth percent. If the extrapolation had been done without considering the infra-red terms, a value too small would have been obtained. It is therefore difficult to explain experimental observations of ϵ which are smaller than the value of n_∞^2 extrapolated from the visible. In the case of CS_2 one would expect ϵ to be larger than such values of n_∞^2 all the more because it has been definitely shown to be the case for its structurally similar compound CO_2. As additional confirmation of the value given here Williams' value of P, as given by Errera,[10] is 22.2 as compared with the value of 22.3_6. The small deviation is in the direction to be expected from data cited by Errera.[12] For the above reasons it is believed that the above mentioned value of $\epsilon = 1.002912$ is about three percent too low.

Molecular Structure

In the previously cited article[1] the authors discussed values for the electric moment of CO, CO_2, COS, and CS_2, with reference to molecular structure. Since in that discussion the moment for CS_2 was tentatively considered to be 0.33×10^{-18} c.g.s. e.s.u., the discussion should be somewhat modified. The moment of COS was found to be 0.65×10^{-18}; and that of CO, 0.10×10^{-18}. Therefore one would expect the moment of CS to be of the same order as that of COS, and the value of the moment of CS_2 as there found would have to correspond to an approximately linear structure, or to a truly linear structure of the unsymmetrical type suggested by Heisenberg. Since the moment of CS_2 is now definitely proven to be zero the situation is simplified. CO_2 has been shown by Stuart[7] to have a rectilinear structure since it has no electric moment and for other reasons which he has pointed out. The similar compound CS_2 has now been shown to have no electric moment, and we can therefore consider with a high degree of probability that its structure is rectilinear.

[10] For an excellent discussion of this see: J. Errera, "Polarization Diélectrique."
[11] O. Fuchs, Zeits. f. Physik **46**, 519 (1928).
[12] Errera, reference 10, p. 68.

THE VARIATION OF DIELECTRIC CONSTANT WITH TEMPERATURE. I. THE ELECTRIC MOMENTS OF THE CARBON BISULPHIDE AND NITROUS OXIDE MOLECULES*

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(Received February 8, 1930)

Abstract

An apparatus has been described which makes it possible to determine dielectric constants of gases and vapors and their dependence on temperature over a range of several hundred degrees. The electric moments of gaseous carbon bisulphide and nitrous oxide have been measured and found to be zero. These results indicate a linear arrangement of the three atoms forming each molecule.

IN RECENT years the study of the constitution of simple polar and non-polar molecules has attracted much attention. There have become available physical methods, among them the dipole theory of Debye,[1] which enable one to determine at least the relative positions of the atoms forming the simpler molecules, and also to say something concerning the symmetry of more complicated ones. In this connection the configuration of the carbon dioxide molecule is of interest. The results of x-ray studies on the solid[2] indicated without any question a linear and symmetrical arrangement of the three atoms which make up the molecule. For a long time, however it was thought that the molecule possessed a finite electric moment, suggesting a triangular arrangement of the atoms for the molecule in the gaseous condition. This conclusion appeared to be substantiated by molecular spectra data, and it was not until Stuart[3] showed its electric moment to be zero that the linear and symmetrical model was accepted for the vapor as well.

There are other triatomic molecules for which electric moment data have been reported in the literature, and in certain cases where rather small values have been reported, the possibility existed that these values were indistinguishable from zero, because of experimental difficulties. Thus an electric moment of magnitude, $\mu = 0.33 \times 10^{-18}$ e.s.u., was reported by Zahn and Miles[4] for the carbon bisulphide molecule, although liquid carbon bisulphide had previously been successfully used as a non-polar solvent for the determination of the electric moment of a number of dissolved molecules.[5] Again,

* This paper is an abstract of a part of the thesis of C. H. Schwingel submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[1] Debye, Handbuch d. Radiologie VI, 597 (1925). Polar Molecules, Chemical Catalog Co., New York, (1929).

[2] Mark, Zeits. f. Elektrochem. **31,** 523 (1925).

[3] Stuart, Phys. Zeits. **47,** 457 (1928).

[4] Zahn and Miles, Phys. Rev. **32,** 497 (1928).

[5] Williams and Ogg, Jr. Amer. Chem. Soc. **50,** 94 (1928).

nitrous oxide shows such a similarity with carbon dioxide in its physical behavior[6] that one might expect it to be non-polar in character as well.

The purpose of this article is to present the results of an experimental study of the temperature variation of the dielectric constant of the vapors of carbon bisulphide and nitrous oxide, and to show that their electric moments do not differ from zero by more than 0.05×10^{-18} in the case of N_2O and by more than 0.02×10^{-18} in the case of CS_2.† The apparatus and method used are briefly described later.

Results

Debye has shown how one may have a dielectric constant, or rather a portion of it that varies with the absolute temperature if it be assumed that there exist permanent electrical dipoles in the molecules. This theory has been amply verified in recent years, so it is only necessary here to give its mathematical result. The total polarization is given by the equation

$$P=\frac{\epsilon-1}{\epsilon+2}\cdot\frac{M}{d}=\frac{4\pi}{3}N\left[\gamma'+\frac{\mu^2}{3kT}\right] \tag{1}$$

where ϵ is the dielectric constant; M the molecular weight; d the density; N is Avogadro's number; γ' is—a constant; μ the electric moment of the molecule; k the Boltzmann constant; T the absolute temperature; $(4\pi/3)\,N\gamma'$ is the polarization due to deformation of the molecule and $(4\pi/3)\,(N\mu^2/3kT)$ is the polarization due to orientation of the molecule. In the case of gases and vapors this equation may be written with sufficient accuracy in the following form:

$$\frac{\epsilon-1}{4\pi}\cdot\frac{M}{Nd}=\gamma'+\frac{\mu^2}{3kT}=a+\frac{b}{T}$$

$$\text{i.e.}\quad \frac{\epsilon-1}{4\pi}\cdot\frac{m\cdot T}{d}=aT+b=D \tag{2}$$

where m = mass of the molecule in question.

In this equation the function D is a linear function of T. The slope of the line gives the polarization due to deformation, while the "y" intercept ($T=0$) gives the value of the electric moment squared divided by $3k$, that is, $b=\mu^2/3k$.

The nitrous oxide used was of hospital purity and triple distilled. It was dried thoroughly with P_2O_5 before each determination.

The carbon disulphide, Baker's C.P. analyzed, was allowed to stand over P_2O_5 for several days before use. On distillation high and low-boiling fractions were discarded. It was later distilled directly into the apparatus.

[6] Langmuir, Jr. Amer. Chem. Soc. **41**, 1543 (1919).

† The experimental work reported herein was practically complete when an article by Ghosh, Mahanti and Mukherjee, Zeits. f. Physik **58**, 200 (1929) appeared in which it was found that both nitrous oxide and carbon bisulphide had zero moments. Thus the results of the two investigations are entirely in agreement.

The results of the experimental work are given by Fig. 1 which has, in turn, been constructed from the data given in Tables I and II. All measurements were made at constant pressure. The simple gas law was used to

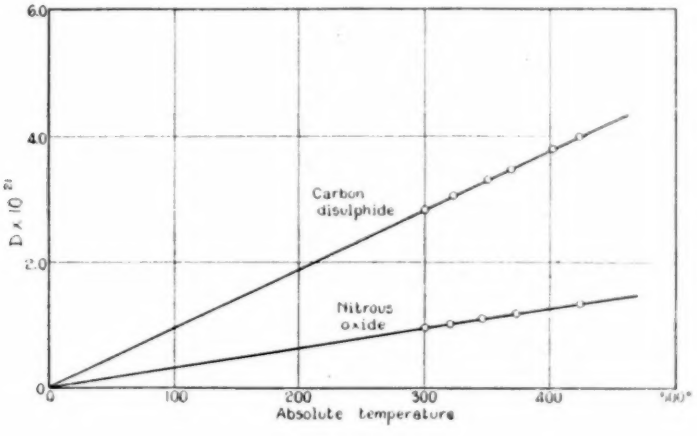

Fig. 1.

calculate the dielectric constant of the gas at 760 mm Hg pressure. The error involved in this method of procedure was proven to be well within the limit of the experimental error of the final result for the electric moments of the molecules.

TABLE I. *Summary of data (Carbon disulphide).*

$T°$	$(\epsilon-1)10^{-5}$ (760 mm)	$D\times10^{21}$	$P=\frac{(\epsilon-1)M}{3d}$
301.6	290	2.84	24.0
322.6	275	3.07	24.2
350.0	250	3.29	23.9
369.8	237	3.45	24.0
400.1	219	3.76	23.9
424.3	206	3.98	23.9

From equation of straight line (Fig. 1), $b=0.001\times10^{-21}=\mu^2/3k$ or $\mu^2=3\times1.37\times0.001\times10^{-37}=0.00041\times10^{-36}$. $\mu=0.020\times10^{-18}$ e.s.u.

TABLE II. *Summary of data (Nitrous oxide).*

$T°$	$(\epsilon-1)10^{-6}$ (760 mm)	$D\times10^{21}$	$P=\frac{(\epsilon-1)M}{3d}$
301.0	993	0.965	8.17
320.5	921	1.02	8.07
347.3	850	1.11	8.10
374.0	780	1.19	8.10
425.6	693	1.35	8.06

From equation of straight line (Fig. 1), $b=0.007\times10^{-21}=\mu^2/3k$ or $\mu^2=3\times1.37\times0.007\times10^{-37}=0.00288\times10^{-36}$. $\mu=0.05\times10^{-18}$ e.s.u.

Experimental Method*

The method used for the determination of the dielectric constants at the various temperatures was similar to that presented by Pungs and Preuner[7] and later improved upon by Zahn,[8] Stuart,[3] Sänger,[9] and others.

Two loosely coupled oscillating circuits, I and II, (Fig. 2) were used to generate constant frequencies, n_1 and n_2. These frequencies, when coupled to a detector, give the frequency $n_d = n_1 - n_2$, which may be detected in the receiver of the detector circuit.

It is evident that a variation of capacity in either circuit will change n_d. If the frequency of circuit II is kept constant, then any change in the frequency of circuit I, due to the change in capacity of C_x, can be detected in

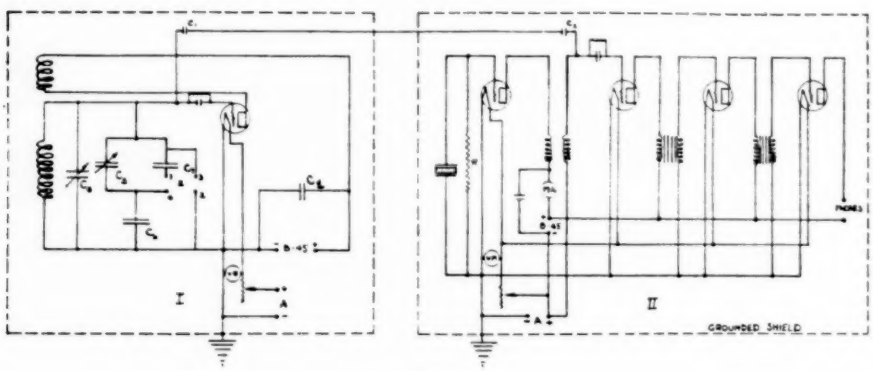

Fig. 2.

the receiver and brought back to the frequency of n_2 by means of a capacity C_s. Circuit I has in series with the gas condenser C_x, a fixed condenser C_y of much greater capacity, and a precision variable condenser C_s. The total capacity is kept constant, determined by the method of counting beats produced in the receivers of the detector circuit. The total capacity of the circuit is changed only by the change in the value of C_x, due to the admission of gases into the previously evacuated condenser; and this is compensated for by means of a change in C_s.

The following equation gives the total series capacity

$$\text{Total capacity} = (1/C_x) + (1/C_y + C_s) \tag{3}$$

If ΔC_x equals the change in capacity due to the admission of gas, and if ΔC_s is the change necessary to bring the circuit to the original frequency of circuit II, then

$$\frac{1}{C_x + \Delta C_x} + \frac{1}{C_y + C_s + \Delta C_s} = \frac{1}{C_x} + \frac{1}{C_y + C_s} . \tag{4}$$

* A diagram of the apparatus without any description was included in an article submitted in June 1929 by one of us (J. W. W.) to the Fortschritte der Chemie, Physik und physikalischen Chemie as part of a discussion of this and related subjects. It is published as Band 20, Heft 5, 1930.

[7] Pungs and Preuner, Phys. Zeits. **20,** 543 (1919).

[8] Zahn, Phys. Rev. **24,** 400 (1924).

[9] Sänger and Steiger, Helv. Phys. Acta. **1,** 369 (1928), et. al.

Solving for ΔC_x, there is obtained

$$\Delta C_x = \frac{C_x^2 \cdot \Delta C_s}{(C_y+C_s)^2+(C_y+C_s+C_x)\Delta C_s} . \tag{5}$$

This can be written with sufficient accuracy

$$\Delta C_x = \frac{C_x^2 \Delta C_s}{(C_y+C_s+\frac{1}{2}\Delta C_s)^2} .$$

If the condenser C_y is very large compared to C_x then a small change ΔC_x will necessitate a large change ΔC_s to bring the circuit to the initial frequency. The frequency of circuit II is kept constant by means of a thermally protected quartz plate.

The electrical connections employed are shown in the figure referred to above. The vacuum tubes were all of the UX 301 type, operated at voltages considerably below rating. It was found that a potential of 4 volts for the oscillating tubes produced the most constant conditions of frequency. The detector tube and amplifiers were operated at full rating. A plate potential of 45 volts was used in all cases. All connections were carefully soldered, and it was found advisable to remove all filament rheostats and voltmeters. The entire apparatus was fastened rigidly in place and thoroughly shielded. Separate shields were used for circuits I and II. Inductances were bakelite tubes wound with silk covered copper wire.

Capacity measurements were made at a frequency of 498.6 kilocycles, corresponding to a wave-length of approximately 600 meters. This frequency was kept constant by means of a quartz crystal, ground and calibrated at the laboratories of the General Radio Company, Cambridge, Mass. For constant conditions of operation, it was found necessary to separate the two circuits by several feet, the only coupling being the single wire as shown in the diagram. Under favorable temperature conditions in the room, the frequency would remain constant to a tenth of a scale division for several minutes, or show a regular increase of several tenths per minute and could be corrected for accordingly. The beats produced in the receiver were amplified by means of two stages of transformer coupled amplification, the zero reading being taken as twenty beats in ten seconds. Capacity C_s was a standard precision condenser of 500$\mu\mu$f capacity, manufactured and calibrated in the laboratories of the General Radio Company. A mica condenser, C_y was calibrated to the latter as standard. All condensers, as well as the entire apparatus, were protected from thermal fluctuations by means of proper insulation.

Gas condenser C_x, was a specially constructed fixed air condenser, made for this particular purpose by the Cardwell Manufacturing Corporation. It is shown diagrammatically in Fig. 3. The construction was of brass and heavily gold plated. The twenty-three plates, each spaced approximately 3 mm, were held in position by means of two strips of Mycalex, the strips being placed as far as possible outside the electrostatic field. The added

capacity correction is negligible, due to their size and position, amounting to not more than 0.2 percent of the total capacity.

This capacity, C_x, was mounted inside a rigidly constructed brass drum (internal diameter, six inches) one terminal of the condenser being grounded to it, and the other leading out through the central glass tube which was used for the entry and removal of gases, and which also contained the thermocouple well. The gas tight drum, containing the condenser, was bolted to the inside of an oil bath, and the capacity when assembled was approximately 444 $\mu\mu$f. The assembly of condenser and thermostat, consisting of (1) thermo-regulator, (2) heater, (3) gas-tight drum, (4) opening for thermocouple, (5) entrance for gas, (6 and 7) condenser terminals, and (8) stirrer, is shown in Fig. 3 and need not be detailed further.

The temperature control bath was a large galvanized iron vessel, insulated completely with "balsam wool," and filled with cotton seed oil. It was kept at constant temperature by means of a heater constructed of nichrome

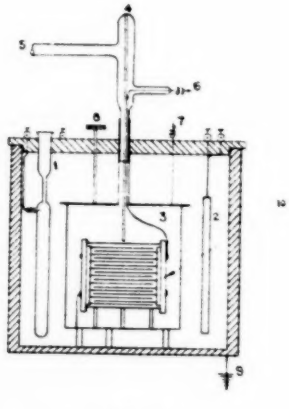

Fig. 3.

wire wound on a grid of "transite." This was immersed directly in the oil. The ordinary make and break type mercury regulator was found satisfactory for keeping the temperature constant to within 0.1° for values up to 100°C, and to within 0.2° for higher temperatures. A calibrated copper-constantan couple placed in close proximity to the condenser served to determine the temperatures. It was found that the temperature became constant after about ten minutes from the time of the gas entry.

In order to evacuate the apparatus, a Hy-Vac oil pump was employed in connection with a water pump. The water pump was used only for the initial clearing out of vapors that might be absorbed by the oil in the pump. In the case of carbon disulphide vapors, and other oil soluble vapors, the system was flushed out thoroughly several times with carbon dioxide, each time evacuating to about 2 cm by means of a water pump. After several of these flushings, the Hy-Vac pump was connected and the system evacuated to 0.01 mm or better. The oil in the pump was changed at frequent intervals. For pressure measurements, a modified U-type manometer was used.

Fig. 4 shows the method used for allowing gases and vapors to enter the condenser chamber. In the case of organic liquids it was necessary to lubricate the stopcocks with a paste made of very finely precipitated silicon dioxide, phosphoric anhydride, and phosphoric acid. This mixture was found to be very satisfactory, having no appreciable vapor pressure, and lasting for the duration of a determination. Outlets *g* and *f* were attached to the oil pump and water pump respectively; and *d* was the connection to the condenser chamber. Stopcock *c* was used to allow the entrance of gases, while *a* was the bulb used for holding the liquids which were allowed to evaporate into the system. Liquids were allowed to evaporate into the system until the partial pressure, as read on the manometer, was slightly less than saturation for room temperature; consequently no condensation could take place in the system.

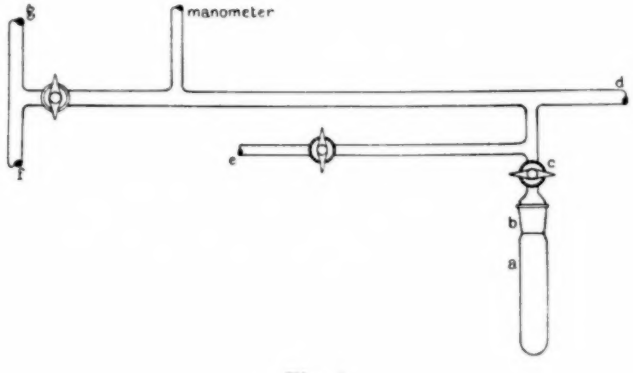

Fig. 4.

To determine the absolute values of the dielectric constants, it was necessary to determine the capacities of all condensers and lead wires.

The capacity of the gas condenser was determined before and after every series of measurements. This was accomplished by means of a mercury switch *z*, Fig. 2. By connecting 1 and 3, the fixed condenser C_y is short circuited. Then C_x and C_s are connected in series and C_s adjusted to fixed frequency corresponding to capacity C_s'. Then C_x was short circuited by connecting 2 and 4, and C_s adjusted to the original beat frequency, or, in other words, until the original capacity had been reached. Calling the new position C_s'', the equation of the series capacity will be,

$$\frac{1}{C_s''}=\frac{1}{C_x+X}+\frac{1}{C_s'} \tag{6}$$

where X is the capacity of the lead wire from C_x to C_s and to *z*. Solving

$$C_x+X=\frac{C_s'\cdot C_s''}{C_s'-C_s''}=C. \tag{7}$$

The value for X, calculated from radio formulae was 10.6 $\mu\mu$f, with a maximum variation of 2 $\mu\mu$f. This amounts to not more than 0.5 percent of the total capacity.

The values for the dielectric constants were calculated according to the equation,

$$\epsilon - 1 = \frac{\Delta C_x}{C - X} \tag{8}$$

where C_x is the capacity before the admission of vapor, including X, the lead capacity.

Combining Eqs. (5), (7), and (8)

$$\epsilon - 1 = \frac{C^2}{(C_y + C_s + \frac{1}{2}\Delta C_s)^2} \cdot \frac{\Delta C_s}{C - X} . \tag{9}$$

Errors in the determination of C_x amount to not more than 0.5 percent, in C_y not more than 1.5 percent, and in ΔC_x not more than 1.5 percent. Since errors in the temperature and pressure measurements are small in comparison, the total error in a dielectric constant determination will not be more than 1.5 percent.

For determining values of ΔC_s, the system was flushed out several times and evacuated. After constant temperature conditions were attained, C_s was adjusted to the beat frequency, twenty in ten seconds. Having taken the reading of C_s', the cock was opened to allow the gas or vapor to enter the condenser chamber. When constant temperature conditions had again been attained C_s was adjusted to the capacity corresponding to the original beat frequency, C_s''. The reading C_s' and the difference between C_s' and C_s'' or ΔC_s were substituted in formula (9), along with predetermined values of C, C_y and X. By this means $\epsilon - 1$ is evaluated directly. Any slight drift in C_s must have been predetermined, and taken into consideration.

For each temperature, five to eight readings were taken, evacuation taking place each time. The time for a single temperature measurement amounted usually to approximately eight hours.

In order thoroughly to test our apparatus the electric moment of the ethyl ether molecule was determined. The result, $\mu = 1.12 \times 10^{-18}$ e.s.u., is in perfect agreement with the recent and now commonly accepted results of Sänger[10] and of Stuart.[11] The electric moment of carbon dioxide was also found to be zero.

Conclusions

The results of this article, with those of Ghosh, Mahanti, and Mukherjee, demonstrate that carbon bisulphide and nitrous oxide do not have finite electric moments.

To explain this fact the simplest assumption is to assign a linear and symmetrical arrangement to the three atoms which form the molecule. It is not our intention, however, to conclude that these are necessarily rigid molecules with which we are dealing. A complete knowledge of the vibration-rotation and rotation spectra of a molecule is also of particular importance in such a study, and these data are unfortunately not available at this time.

[10] Sänger, Leipziger Vorträge, 1929.

[11] Stuart, Zeits. f. Physik **51**, 490 (1928).

THE NUMERICAL DETERMINATION OF CHARACTERISTIC NUMBERS

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(Received February 24, 1930)

Abstract

A method is developed for the numerical calculation of characteristic energy levels in cases where the wave equation contains, or can be reduced so as to contain, a single space variable. The procedure consists in the numerical integration of an auxiliary differential equation for several chosen values of the energy, after which the characteristic values are obtained by interpolation. The method is one of considerable generality so far as the form of the differential equation is concerned, and is capable of giving any preassigned degree of accuracy.

1. The entrance of wave mechanics into modern physics gives new interest to boundary value problems associated with linear differential equations, especially those problems treated by Weyl[1] and others which have to do with the Sturm-Liouville equation

$$\frac{d}{dx}\left[p(x)\frac{dy}{dx}\right] - q(x)y + \lambda\rho(x)y = 0 \tag{1}$$

in the intervals $0<x<\infty$ or $-\infty<x<\infty$. A problem of particular physical interest is the determination of those characteristic values of λ (eigenwerte) for which (1) possesses solutions that are finite at both ends of the interval.[2] In several important special cases the complete analytical solution of this problem is known,[3] but in other instances it is necessary to resort to approximate methods.

The object of this note is to describe a numerical procedure for obtaining the characteristic values of λ belonging to the equation

$$\frac{d^2u}{dx^2}+G(x,\lambda)u=0. \tag{2}$$

Equation (1) can be reduced to this form by the substitution $y=up^{-1/2}$, provided p has first and second derivatives and does not vanish in the interval.

[1] Weyl, Mathematische Annalen **68,** 220 (1910), and Göttinger Nachrichten, (1910), p. 442. Hilb, Mathematische Annalen **76,** 333 (1915). Milne, Trans. Amer. Math. Soc. **30,** 797 (1928).

[2] Schrödinger, Ann. d. Physik **79,** 361 (1926). See p. 363. Kemble, Phys. Rev. Supplement **1,** 157 (1929), see p. 177.

[3] Cf. e.g. Kemble, reference 2, pp. 183–186. Condon and Morse, Quantum Mechanics, (McGraw-Hill, 1929) Chapter II.

Equation (2) contains as a special case the wave equations of the type

$$\frac{d^2u}{dx^2}+\frac{8\pi^2\mu}{h^2}[W-V(x)]u=0, \tag{3}$$

as is seen by setting

$$\lambda=\frac{8\pi^2\mu W}{h^2}$$

and

$$G(x,\lambda)=\lambda-\frac{8\pi^2\mu}{h^2}V(x).$$

Equation (2), however, is considerably more general than (3).

With regard to $G(x,\lambda)$ we assume that $\partial G/\partial\lambda$ exists and is positive, that $G(x,\lambda)$ is continuous in x, that when $|x|$ is sufficiently large $G(x,\lambda)$ is negative for the values of λ under consideration, and (if the interval is $0<x<\infty$) $\lim_{x=0} G(x,\lambda)=-\infty$.

2. For simplicity we consider only the case in which the interval is $-\infty<x<\infty$. Let x_0 be a value of x in the interval, and let $u_1(x)$ and $u_2(x)$ be two solutions of Eq. (2) satisfying the conditions

$$\begin{aligned} u_1(x_0)&=1, & u_2(x_0)&=0,\\ u_1'(x_0)&=0, & u_2'(x_0)&=a\neq 0. \end{aligned} \tag{4}$$

The constant a is arbitrary and in any particular case is to be determined so as to make the numerical work as simple as possible. These solutions satisfy the well-known identity

$$u_1(x)u_2'(x)-u_2(x)u_1'(x)\equiv a. \tag{5}$$

Let a function $w(x)$ be defined by the equation

$$w(x)=[u_1^2(x)+u_2^2(x)]^{1/2} \tag{6}$$

By differentiating this equation twice, eliminating $u_1''(x)$ and $u_2''(x)$ by means of (2), and simplifying with the aid of (5) we find that the function $w(x)$ satisfies the simple differentiation equation

$$\frac{d^2w}{dx^2}+G(x,\lambda)w-\frac{a^2}{w^3}=0. \tag{7}$$

Now the general solution of (2) can be expressed in the form

$$u(x)=Cw(x)\sin\left\{a\int_{x_0}^{x} w^{-2}dx-\alpha\right\}, \tag{8}$$

in which C and α are arbitrary constants. Since with the given hypotheses $w(x)$ does not approach zero at either end of the interval, it is clear that a solution satisfying the desired conditions at both ends of the interval can be found if and only if

$$\frac{a}{\pi}\int_{-\infty}^{\infty} w^{-2}dx = n \tag{9}$$

in which n is a positive integer.

3. Now the integral

$$N = \frac{a}{\pi}\int_{-\infty}^{\infty} w^{-2}dx \tag{10}$$

is an increasing function of λ, so that if we select k values of λ for which this integral is finite (values of λ for which N is infinite belong to the continuous spectrum and do not interest us here), say $\lambda^1 < \lambda^2 \cdots < \lambda^k$, we obtain k values of N, say $N_1 < N_2 \cdots < N_k$. If an integer n lies in the interval $N_1 < n < N_k$, we may use the method of interpolation to obtain approximately the corresponding value of λ, $\lambda = \lambda_n$, which will be precisely the n-th characteristic value of λ counted in order of magnitude.

To put this plan into execution we proceed as follows:

First, we solve Eq. (7) with the initial conditions $w(x_0) = 1$, $w'(x_0) = 0$ for each of the k values of λ, $\lambda,^1 \lambda^2 \cdots \lambda^k$. For this purpose we may use any one of several well-known methods for the numerical integration of differential equations.

Second, using in turn each of the solutions now obtained, we evaluate by numerical quadrature the integral (10) and get the k values of N, N_1, $N_2, \cdots, N_k$.

Lastly, we obtain by interpolation the values of λ corresponding to each integer in the interval N_1 to N_k.

When the characteristic value of λ has been found it is then possible to integrate (7) using this value of λ and then obtain the corresponding wave function itself by means of (8). As a matter of fact, however, it will generally be easier to obtain $w(x)$ and $\int_0^x w^{-2}\,dx$ by interpolation from the computations already performed.

Naturally the speed and accuracy of the method depend largely on good judgment in the selection of the trial values $\lambda^1, \lambda^2 \cdots \lambda^k$. This is perhaps best illustrated by means of an example.

4. We take as an illustrative example the differential equation

$$\frac{d^2u}{dz^2} + \frac{8\pi^2\mu}{h^2}[W - kz^4]u = 0,$$

which upon the substitutions

$$z = \frac{h^{1/3}}{(8\pi^2\mu k)^{1/6}}x,$$

$$\lambda = \left[\frac{64\pi^4\mu^2}{h^4 k}\right]^{1/3} W,$$

reduces to

$$\frac{d^2u}{dx^2}+(\lambda-x^4)u=0.$$

For simplicity we choose $x_0=0$, $a=\lambda^{1/2}$, so that equation (7) becomes

$$\frac{d^2w}{dx^2}+(\lambda-x^4)w-\lambda w^{-3}=0, \tag{11}$$

with the initial conditions $w=1$, $w'=w''=w^{(3)}=w^{(4)}=w^{(5)}=0$ at $x=0$. The desired solution is even, so that we need to compute it for positive values of x only.

The critical values of λ are evidently positive, and when n is large their order of magnitude can be obtained from the formula[4]

$$\pi n=\lambda_n^{3/4}\int_0^1 s^{1/4}(1-s)^{-1/2}ds+R_n,$$

in which R_n is bounded. This gives

$$\lambda_n=n^{4/3}[2.184+E/_n]$$

where E is bounded. It appears, therefore, that λ_1 will probably lie somewhere between 1 and 4, so we choose the four trial values $\lambda^1=1$, $\lambda^2=2$, $\lambda^3=3$, $\lambda^4=4$, and calculate the solution of (11) for each of these values. The method actually used was that described by the author elsewhere.[5] With the aid of a calculating machine and Barlow's Tables the integration can be done rapidly. The values of $1/w^2$ and $1/w^3$ are read directly in the columns headed "square" and "cube" respectively. We retained only enough significant figures in w to give $1/w^2$ to four places of decimals. The first one of the four computations is shown below to illustrate the general method. The integrals

$$I(\lambda)=\int_{-\infty}^{\infty}w^{-2}dx=2\int_0^{\infty}w^{-2}dx$$

were found with the calculating machine, using Weddle's rule and were checked with Simpson's rule. They proved to be as follows:

λ	$I(\lambda)$	ΔI	$\Delta^2 I$	$\Delta^3 I$
1	3.0469			
		621		
2	3.1090		8	
		629		6
3	3.1719		14	
		643		
4	3.2362			

[4] Milne, Trans. Amer. Math. Soc. **31,** 907–918 (1929), see formula (25) p. 914.

[5] Milne, Numerical Integration of Ordinary Differential Equations, Amer. Math. Monthly **33,** 455 (1926).

From (8), since $a=\lambda^{1/2}$, we get

$$\lambda_n=[\pi n/I(\lambda)]^2$$

and by a few trials find from this that the values of the first two characteristic numbers are

$$\lambda_1=1.0605$$

$$\lambda_2=3.7998.$$

COMPUTATION I. $\lambda=1$.

x	w	w'	w''	$[x^4-1]$	$1/w^3$	$1/w^2$
0	1.0000	.0000	.0000	−1.0000	1.0000	1.0000
.1	1.0000	.0000	.0001	−.9999	1.0000	1.0000
.2	1.0000	.0001	.0016	−.9984	1.0000	1.0000
.3	1.0000	.0005	.0081	−.9919	1.0000	1.0000
.4	1.0001	.0021	.0252	−.9744	.9997	.9998
.5	1.0005	.0061	.0605	−.9375	.9985	.9990
.6	1.0015	.0151	.1238	−.8704	.9955	.9970
.7	1.0038	.0322	.2258	−.7599	.9886	.9924
.8	1.0084	.0620	.3798	−.5904	.9752	.9833
.9	1.0168	.1104	.6016	−.3439	.9513	.9673
1.0	1.0314	.1853	.9114	.0000	.9114	.9400
1.1	1.0551	.2966	1.341	.4641	.8514	.8983
1.2	1.0924	.4590	1.940	1.0736	.7671	.8380
1.3	1.1493	.6930	2.792	1.8561	.6587	.7570
1.4	1.2344	1.031	4.039	2.8416	.5316	.6563
1.5	1.3606	1.522	5.924	4.0625	.3971	.5402
1.6	1.5467	2.251	8.859	5.5536	.2703	.4181
1.7	1.8232	3.353	13.57	7.3521	.1650	.3008
1.8	2.2377	5.067	21.34	9.4976	.0893	.1997
1.9	2.8706	7.803	34.58	12.0321	.0423	.1213
2.0	3.856	12.32	57.83	15.0000	.0175	.0673
2.1	5.440	20.01	100.4	18.4481	.0062	.0338
2.2	8.058	33.66	180.7	22.425	.0019	.0154
2.3	12.60	58.74	338.6	26.98	.0005	.0063
2.4	20.57	106.9	661.6	32.18		.0024
2.5	36.5	230.0	1387.	38.06		.0007
2.6	60.	410.0				.0003

$\int_{-\infty}^{\infty} w^{-2}dx=3.0469$ by Weddle.
3.04688 by Simpson.

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Growth of Zinc Crystals

In two recent papers by Goetz and Hasler[1] and Goetz[2] reference is made to a paper by Mr. A. G. Hoyem[3] and myself on the growth of zinc crystals. Since certain conclusions are drawn which are based on a misconception of one point in our work I would like to point out that for crystals of the same diameter, drawn at the same rate, the height of the column of liquid zinc just below the crystal is *always the same*, regardless of the temperature of the molten zinc. It is of course obvious that the higher the latter temperature the greater the blast of cooling gas that must be used. Too feeble a gas blast for the molten zinc temperature causes an increase in the height of the liquid zinc column but also a *reduction of the diameter of the crystal*. Mr. Hoyem and I therefore felt justified in considering the excess of temperature of molten zinc (in the crucible) above the melting point of zinc as proportional to the temperature gradient in the liquid column as long as crystals of only one diameter were grown and at a single rate. Our paper would have had little point otherwise.

E. P. T. TYNDALL
Department of Physics,
University of Iowa
March 7, 1930

[1] A. Goetz and Maurice F. Hasler, Proc. Nat. Acad. **15**, 646 (1929).
[2] A. Goetz, Phys. Rev. **35**, 193 (1930).
[3] A. G. Hoyem and E. P. T. Tyndall Phys. Rev. **33**, 81 (1929).

The Spark Spectrum of Ruthenium

During last year we undertook the analysis of the spectrum Ru II. The fundamental multiplets were very easily discovered, but further progress was stopped by the insufficient accuracy of the measures. Accurate measures will shortly be made and the analysis extended. In the meantime it is perhaps of interest to give a table of the low terms. The table includes the electron configuration, designation and value of each low term. The odd terms are not given, but comprise $^6P^\circ$, D°, F° and $^4P^\circ$, D°, $F^\circ(d^6p)$.

Table of low terms of Ru II.

d^7	$^4F_{4\frac{1}{2}}$	0.0
"	$^4F_{3\frac{1}{2}}$	1523.0
"	$^4F_{2\frac{1}{2}}$	2494.0
"	$^4F_{1\frac{1}{2}}$	3104.2
"	$^4P_{2\frac{1}{2}}$	8256.8
"	$^4P_{1\frac{1}{2}}$	8477.4
d^6s	$^6D_{4\frac{1}{2}}$	9151.5
d^7	$^4P_{\frac{1}{2}}$	9373.6
d^6s	$^6D_{3\frac{1}{2}}$	10150.6
"	$^6D_{2\frac{1}{2}}$	10851.8
"	$^6D_{1\frac{1}{2}}$	11303.6
"	$^6D_{\frac{1}{2}}$	11604.1
"	$^4D_{3\frac{1}{2}}$	19378.7
"	$^4D_{2\frac{1}{2}}$	20514.9
"	$^4D_{1\frac{1}{2}}$	21246.2
d^7	$^2F_{2\frac{1}{2}}$	21557.8
d^6s	$^4D_{\frac{1}{2}}$	21645.5
d^7	$^2F_{3\frac{1}{2}}$	22289.0

Measurements of the Zeeman effect indicate that the g-values are very close to the normal Landé values.

It will be noticed that $(d^7)^2F$ is reinverted as is predicted by Goudsmit's theory.

W. F. MEGGERS
A. G. SHENSTONE
March 11, 1930

X-Rays Generated by Three Element Tube

The character of the x-rays generated by a specially designed three element tube was studied. This tube consisted of two filaments placed symmetrically with respect to a ring anode. The two filaments were maintained at the same potential and the electrons accelerated to the anode by a high voltage, 15,000 volts A.C. in these experiments, applied between the filaments and the anode. When the filament current was increased sufficiently, the anode current became limited by space charge and the tube started to oscillate; in this condition, the electrons oscillate back and forth through the anode.

While oscillations were present, the tube became a very efficient producer of x-rays, in the anode region. The average wave-length of these x-rays, as measured by their absorption coefficient in thin metal foils was less than 0.8A. This indicates that either the efficiency of exciting continuous x-rays with a wave-length corresponding to the full voltage applied to the electrons is very great or that the tube can emit x-rays with a wave-length shorter than that calculated from the voltage impressed between the anode and the filaments. The hardness of the x-rays may be due either to very high voltage oscillations in the tube which increases the energy of the electrons striking the anode or it may aise from the mutual interaction of the electron streams from the two filaments in the space surrounding the anode where the electron concentration is very high. A pin-hole picture of the source of the x-rays showed that the x-rays were generated in a space charge sheath surrounding the glass wall and extending into the space around the anode. In all these measurements, the pressure in the tube was less than 10^{-6} mm of Hg.

With one filament heated, i.e. no oscillations in the tube, no x-rays could be detected for the same anode current and voltage.

ARTHUR BRAMLEY

Bartol Research Foundation
Swarthmore, Pa.
March 8, 1930.

Regularities in Radioactive Nuclei

While reading an interesting paper by Barton (Phys. Rev. **35,** 408 (1930)) on "A New Regularity in the List of Excited Nuclei," it occurred to us that it would be interesting to look for a similar regularity in radioactive nuclei. (The symbols we shall use in discussing this addition to his work will be those of Barton's paper, and for brevity will not be redefined here.) We plotted P against E for these nuclei assuming that the mass numbers of the actinium family are secured from those of uranium 238 by the subtraction of an integral number of α particles with mass number 4. Plotted in this way an approximate center of symmetry exists at (P, E) equal to (220, 134) which is thorium emanation. There are 34 points in this diagram, some of which are double because two radioactive nuclei fall at the same point in a number of cases. It is necessary to add 5 points to the diagram in order to complete the symmetry so that the symmetry of this "cluster" compares favorably with Barton's non-radioactive clusters. It seems, therefore, that we are justified in adding another cluster to the three which he found. The uranium-radium-actinium family and the thorium family each form independent symmetrical clusters about the same point.

There is some uncertainty as to whether the mass number of a protactinium should be 230 as we have assumed it to be, 231, or 232. If its mass number should be 232, the actinium family and the thorium family diagrams would coincide except that (232, 141) must be added to the thorium family and (228, 140) must be added to the actinium family, and thus the actinium and thorium families would be symmetrical about the point (220, 134). The uranium-radium family would be approximately symmetrical about the point (224, 137), but the symmetry would not be so great as it is when all families are plotted together with the protactinium taken with mass number 230. If protactinium is taken with mass number 231 then the actinium family will be symmetrical about (219, 133), the thorium family would be symmetrical about (220, 134), and the uranium-radium family would have its lesser symmetry about the point (224, 137); but if all families were plotted on the same dia-

gram, the appearance of symmetry would be destroyed. It seems that all these families should be plotted on the same diagram in order to make comparisons with Barton's clusters which include all possible "radioactive families" of these non-radioactive elements.

Assuming for the sake of argument that this radioactive cluster exists, it indicates that Barton's suggested mechanism for the origin of his clusters is improbable, for his mechanism cannot be applied to the radioactive cluster. A primordial element of mass number 440 and 268 nuclear electrons cannot be postulated. Moreover, we know that the radioactive atoms do not originate by the decomposition of such a primordial element. The symmetry of this cluster is determined by regularities in the radioactive decomposition series and, therefore, the suggestion immediately arises that Barton's clusters may consist of radioactive series of nuclei with very long lives. From Aston's data (Proc. Roy. Soc. **A115,** 487 (1927)) on packing fractions, it is easy to see that considerable radioactivity might be possible in the (124, 72) cluster because for the general decreasing packing fractions with decreasing mass number in this region. Only a very feeble radioactivity or none at all would be possible in the (80, 45) clusters because these atoms are so near the minimum of the packing fraction curve. Rubidium whose isotopes are (85, 48) and (87, 50) and belong to this cluster has been reported to be slightly radioactive. The lowest cluster with center at approximately (25, 13) could not be radioactive at all because the packing fraction curve has a negative slope. It seems to us that the symmetry of these 4 clusters is probably not due to the process of formation of the nuclei at all, but merely represents some stability relationship or some nuclear exclusion principle. At sufficiently high temperatures and pressures atoms of high packing fraction and high mass number would be stable and probably in the genesis of the elements under such conditions the possible permitted nuclei would be formed. In the radioactive cluster we merely see a spontaneous process which results in a transient excitation of these same possible permitted nuclear configurations.

It is interesting to note that the centers of these 4 clusters are at atomic numbers 12(?), 35, 52 and 86 which are very near the atomic numbers of the inert gases neon, krypton, xenon and the emanations. We have no idea whether this approximate agreement has any significance.

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March 22, 1930.

BOOK REVIEWS

The Kinematical Design of Couplings in Instrument Mechanisms. A. F. C. POLLARD, A. R. C. S., A. M. I. E. E., Professor of Instrument Design at the Imperial College of Science and Technology. Pp. 64, figs. 25. Adam Hilger, Ltd., London, England, 1929. Price 4s. 6d.

This book is an application to instrument design of the law of kinematics that six constraints are necessary to fix a rigid body. The author defines the terms used in the book, states the principles of kinematical design, and cites examples of the application of these principles to the design of instruments recently built by Adam Hilger Ltd., W. G. Pye and Co., Cambridge Instrument Co., E. Leitz, and others. Machine tool design of instruments depends too largely on the machines used in construction and on past experience, too little on kinematical principles, whereas kinematical design places first importance on these principles. By the latter method the forces on various members of an instrument are determined, the proper number of constraints applied, the materials decided upon, the so-called point contacts on the guiding surfaces expanded to withstand the pressures involved, and the allowable fits or clearances determined. This results in a stable instrument, in a reduction of variance in the instrument, in simpler and more economical manufacture because the workmanship is expended in the production of accurate geometrical forms rather than accurate fits, and permits the introduction of small adjustments which are often of great importance. Though this book is not intended as a complete text, it adequately sets forth the principles of the subject. It should be of great value to those who construct, repair, or use precision instruments.

Since reading the book this reviewer has applied these principles to the design of a comparator and an adjustable lamp support for the recording galvanometer of a microphotometer. A study of some of our present apparatus indicates that changes indicated by kinemantical design would be very desirable. Accurate steel balls, which are easily and cheaply procurable, are widely used in these designs.

C. W. GARTLEIN

Handbuch der Experimentalphysik, Vol. IX, Part 1. High and Low Temperature by H. VON WARTENBERG; Liquefaction of Gases by H. LENZ; Heat Conduction by OSCAR KNOBLAUCH and H. REIHER; Heat Radiation by W. WIEN and C. MÜLLER. Pp. 484, figs. 50. Akademische Verlagsgesellschaft, Leipzig, 1929. Price, bound RM 44.60.

The first section by Wartenberg is a detailed listing of the means for obtaining and methods of measuring high and low temperatures.

The second section by Lenz on the liquefaction of gases is a very excellent discussion, both qualitative and quantitative, of the whole problem. The thermodynamic aspect of the fundamental gas theory is given in detail. The literature of the experimental side of the theory is completely given with interesting abstract and comment. The experimental work and data for air are given particular attention and their application to the liquefier problems carried right through. The writer knows of no such treatment anywhere in English.

The various technical methods used for liquefying air are described in their physical, not their engineering aspect. The liquefaction of H and He are described in connection with the actual installation at the few places where they have been carried out.

A short treatment on separation or purification of gases by fractional distillation—oxygen and nitrogen from air, hydrogen from various mixtures, helium from natural gas—completes the section.

The section on heat transfer is opened by Oscar Knoblauch with a discussion on heat conduction. After a brief introduction to the analytical situation, the experimental methods with some results are described for the metals especially with reference to the Wiedeman and Franz relation; for poorly conducting bodies with special reference to economically important materials; for single crystals, for liquids and for gases.

The second part, heat transfer by convection (Reiher), covers the very complex and important subject especially in its engineering aspect of the transfer of heat between solid bodies by a moving fluid. Both the analytical and experimental aspects are given in considerable detail, especially the case of transfer through tubing in various arrangements.

The third part discusses radiation as a means of heat transfer without duplication seriously of the later section. The fourth part discusses some important applications of the previous discussion.

The third and final section of the volume is by W. Wien and C. Müller on heat radiation, of which Wien writes the larger part. They cover the general theory, thermodynamical and statistical; experimental technique, sources, measuring instruments, units, black body, light pressure; experimental test of the theory and measurement of the radiation constants; energy distribution in the spectrum. The mass of references seems to cover all the important work.

J. R. ROEBUCK

Wave Mechanics, Being One Aspect of the New Quantum Theory. H. T. FLINT. Pp. ix+117. E. P. Dutton, New York. Price, $1.25.

This little book, which has just (March 1930) been received for review has a preface dated December 1928. It is probably the poorest of the books which have appeared on this subject. It is of about the scope of Biggs' little book on wave mechanics.

Chapter 1 and 2 present the analogy between optics and mechanics and arrive at the wave equation in much the same way as Schrödinger did in the second of his famous series of Annalen der Physik papers.

The Schrödinger relativistic equation is given and the erroneous formula for the hydrogen fine structure to which it leads is presented. Then the author says, "It is apparently of no purpose to discuss the accuracy of the formula just obtained . . . . " and does not tell the reader that the formula is wrong and how the electron spin hypothesis corrects it and improves Sommerfeld's original theory of the fine structure!

Chapter 4 purporting to review the diffraction by crystals and gases of electron waves, is very bad. Three of the book's 19 figures are devoted to the old uncertain results of Davisson and Kunsman while not a single mention is made of the work of Davisson and Germer! Then three more figures are devoted to Dymond's work on scattering in helium although Harnwell had shown that these results were due to secondary effects and published his work during 1928. Then follow about ten pages about G. P. Thomson's electron diffraction work still with no reference to the earlier work of Davisson and Germer.

The last fifth of the book is devoted to an account of attempts to connect Ψ with the general relativity theory which are certainly among the least important of the recent developments especially since they were carried out without reference to the electron spin problem which Dirac showed (winter, 1927) was inseparably connected with relativistic effects. I can find no mention of electron spin in the whole book.

Now the reason for setting these things out so fully is this: The publishers wrote to me a year ago for criticism of this book and paid me well for it. I told them much the same as I have written here and recommended that the book be revised before being issued in this country. But I suppose that was to much trouble so they prefer to offer to the physicists of America, at a price of more than 1 cent per 8×14 cm type page, a book which is very much out of date, misleading in spots, and ignores completely one of the finest pieces of experimental work done in the past decade.

E. U. CONDON

Bandenspektren auf experimenteller Grundlage. RICHARD RUEDY. Pp. vi+124, figs. 62. Sammlung Vieweg, Heft 101/102, 1930. Price RM 9.60.

Progress in the field of band spectra, since the publication, in 1926, of the National Research Council Bulletin "Molecular Spectra in Gases," has been both extensive and important. As a result, there is a real demand for an up-to-date account, but the knowledge and the time required to prepare a really adequate monograph on this very complex subject are

so great that even the leading workers in the field have shrunk from the task. The volume under review cannot be said to satisfy the demand. It is written in text book style,—that is, categorically, with no references to original literature, save for a brief list on the last two pages, of which no mention is made elsewhere. The reviewer feels that the subject is still too new for this style of treatment, and that the general reader is likely to get a false impression from it. A large portion of the volume is devoted to a detailed description of the fine structure, of various types of bands. This will be of interest mainly to the prospective research worker but the precise definitions and directions, so necessary for successful work, are in general not included. The most valuable feature of the book is the many diagrams, mainly taken with more or less adaptation from the original literature.

The nomenclature of band spectra is now undergoing a complete revision, and preliminary evidences appear in this volume, where two different symbols for the same quantity are sometimes used indiscriminately. In this matter of nomenclature, just one point will be mentioned. It has recently been agreed to use v as the vibrational quantum number (the former n). Professor Mulliken and the reviewer are now suggesting the use of $u=v+1/2$, so that $u=0$, or $v=-1/2$, for the hypothetical state of zero vibration. Ruedy retains n with its former meaning, and defines $v=n+1/2$, so that his v is our u. He then makes the error of defining *his* v as the vibrational quantum number.

RAYMOND T. BIRGE

Handbuch der Experimental Physik, Band VIII, 2. Teil. Wärmeausdehnung, Zustandsgrössen und Theorien der Wärme. Pp. xii+766, 17.1×24.1 cm, Akademische Verlagsgesellschaft M. b. H., Leipzig, 1929. Price, bound RM 76.

Not much more can be attempted in a necessarily short review of a book of this character and extent than a summary of the nature of the contents.

The thermal expansion of solids and liquids is treated in 72 pages by Valentiner. Not only are the conventional experimental methods described with the aid of a number of diagrams but the theoretical significance of such measurements is made plainer by a discussion of the laws of expansion proposed by Debye and Grüneisen.

The thermal parameters (Thermische Zustandsgrössen) of gases at moderate and low pressures are discussed by Otto in an article of 161 pages. This includes a discussion of the experimental methods of determining the p-v-t relations for gases, together with the experimental results, dealing particularly with the experiments of Amagat. There is a very useful section on equations of state, with a reproduction of the 56 most important such equations that have been proposed. A very short section is given on gaseous mixtures.

The thermal parameters of liquids, solids and gases under high pressures are treated in 155 pages in an article written by myself and translated by Lenz. This article is by intention mostly concerned with my own experiments, and deals with the compressibility of liquids, gases, and solids as a function of pressure and temperature, melting phenomena and polymorphic transitions under high pressure. There is a short concluding section on the absorption of gases by liquids at pressures of a few hundred kg/cm².

Adsorption phenomena of gases and vapors on solid surfaces are treated in 100 pages by Glaser. Not only is the experimental material presented, but there is a welcome discussion of the thermodynamics of adsorption.

Vapor pressure measurements are discussed in 76 pages by Harteck. This includes the conventional material, and also such recent material as methods of determining the vapor pressure of involatile substances like tungsten or carbon. There is a section on hygrometry, which perhaps might not be looked for under the general heading.

The kinetic theory of gases and vapors is treated in 144 pages of Przibram. Such an article on a theoretical subject might perhaps not be expected in a Handbuch ostensibly devoted to experimental topics, but the emphasis is throughout on the experimental aspects, and for this reason it will be found to be a most useful supplement to the ordinary theoretical discussions by statistical methods. The discussions of recent direct methods of determining the actual velocity of gas molecules and demonstrating the Maxwellian velocity distribution are to be especially commended.

The concluding article is a short one of 22 pages by Herzfeld on certain consequences for physical chemistry of Nernst's heat theorem, dealing mostly with transition and reaction phenomena, with a discussion of the chemical constant.

P. W. BRIDGMAN

Molecular Spectra and Molecular Structure. A General Discussion held by the Faraday Society, September 1929. Price 15/6.

This volume consists of a collection of forty papers on molecular spectra and molecular structure given before the Faraday Society, September 1929, at the University of Bristol. The contributions are grouped into three parts, Band Spectra in the Visible and Ultra-Violet Regions, The Raman Effect and Infra-Red Spectra which latter part is subdivided into sections dealing with Solid Bodies, Liquids and Gases. Each division is opened by an introductory paper which presents the subject and gives something of the historical development. This is then followed by a series of original papers dealing with researches on particular phases of the problem.

It is difficult to summarize the individual papers since the problems they treat are so diversified. The reviewer can only call attention to some few which appear to him to be more outstanding. In the first section we find an attempt to provide a uniform Nomenclature for Diatomic Molecular Spectra introduced by O. W. Richardson, Band Spectra and Atomic Nuclei by R. S. Mulliken, a paper on Chemical Binding by F. Hund, a general paper on the Electronic Structure of Diatomic Molecules by J. E. Lennard-Jones and papers describing particular diatomic molecules by R. C. Johnson, O. W. Richardson, and W. E. Curtis. R. T. Birge contributes two papers, The Determination of Heats of Dissociation by Means of Band Spectra and Recent Work on Isotopes in Band Spectra.

The second part is opened with a paper by Professor Sir. C. V. Ramen and is followed among others by articles by R. W. Wood and J. C. McLennan. The section on Infra-Red Spectra is well represented by some thirteen papers including, On the Infra-Red Spectra of Gases under High Dispersion by E. F. Barker and C. F. Meyer, and The Absorption Spectrum of Ammonia Gas in the Near Infra-Red by R. Mecke and R. M. Badger.

This volume issued by the Faraday Society will prove useful in three ways. The introductory articles are for the most part excellent and serve as a survey of the whole field of molecular spectra. The original contributions are valuable as such and give a good account of the most recent work on the subject. All the papers seem to be well supplied with citations of earlier work and since there are so many of them, on so many different phases, the whole collection may profitably be used for purposes of reference.

DAVID M. DENNISON

The Science of Voice. DOUGLAS STANLEY. Pp. 327, Carl Fisher Inc., 430 S. Wabash Avenue, Chicago. 1929.

This book was apparently written principally for the use of teachers and students of singing and speaking. It is divided into three parts. First, a physical introduction written in rather elementary form and in such a way that teachers and students with a moderate understanding and interest in physical principles might profit by it. The second part called "Vocal Technic" contains a description in physical terms of what the author considers to be a mechanism of the various terms used in vocal art. For a physicist without musical experience who is interested in the meaning attached by musicians to such terms as "register," "breath control," "the vibrato," "slur," "shakes," "staccato," etc., this second section is very suggestive in a manner which seems to be unique in such treatises. The third section on "musicianship and interpretation" is addressed almost entirely to musicians.

R. L. WEGEL